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Influence of Sol-Gel Process Parameters on Structural Properties of CuO Nanoparticles

Sol-Jel Proses Parametrelerinin CuO Nanopartiküllerin Yapısal Özelliklerine Etkisi

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ABSTRACT

The production of nanostructures by different methods and their use in many application areas have become very important in recent years due to the rapid development of technology. Metal oxide nanostructures attract considerable attention with their utilization as catalysts in chemical industries and in electronic and photonic devices. Nanomaterials in the form of nanoparticles are in demanded by the chemical industry as a result of their superior properties. Among the metal oxides, CuO nanoparticles are of specific interest in catalysis, magnetic storage media, gas sensors, batteries and solar transformer applications owing to their p-type semiconductor and narrow band gap, which varies depending on fabrication conditions. In addition, CuO nanoparticles are widely used as a strong heterogeneous catalyst especially in chemical sensor applications because of its high activity and selectivity in oxidation and reduction reactions. Several methods have been used to synthesize CuO nanoparticles. Among these, sol-gel technique facilitates the production of crystalline nanomaterials with various morphologies and sizes, especially by changing parameters such as temperature, reaction time, pH of the sol solution and concentration of reagents. The aim of this study is to investigate the influence of pH of the sol and calcination temperature on the structural and morphological properties of sol-gel synthesized CuO nanoparticles. The synthesized CuO nanoparticles were characterized by using X-ray diffraction (XRD), scanning electron microscopy (SEM), dynamic light scattering (DLS) and Fourier transform infrared spectroscopy (FTIR). XRD results revealed that synthesized nanoparticles were monoclinic CuO crystal structure without any impurity. The mean crystallite size of nanoparticles was calculated using the Scherrer formula and found in the range of 20 - 30 nm. Additionally, FTIR spectroscopy analysis also affirmed the formation of pure copper oxide nanoparticles. Our findings confirm that investigated process parameters had an effect on the structural and morphological properties of the synthesized CuO nanoparticles.

Keywords: Metal Oxide, CuO, Nanoparticle, Sol-Gel, Calcination Temperature, pH Effect

ÖZET

Son yıllarda teknolojinin hızla gelişmesi nedeniyle farklı yöntemlerle nanoyapıların üretilmesi ve birçok alanda kullanılması önemli hale gelmiştir. Metal oksit nanoyapıların kimya endüstrilerinde, elektronik ve fotonik cihazlarda katalizör olarak kullanımı büyük ilgi görmektedir. Nanopartikül formundaki nanomalzemeler, üstün özellikleri nedeniyle kimya endüstrisinde talep görmektedir. Metal oksitler arasında, bakır oksit nanopartiküller p-tipi yarı iletken olmaları ve üretim koşullarına bağlı olarak değişen dar bant aralıkları nedeniyle, kataliz, manyetik depolama ortamları, gaz sensörleri, piller ve güneş transformatörü uygulamalarında özellikle ilgi çekmektedir. Ayrıca oksidasyon ve indirgeme reaksiyonlarındaki yüksek aktivitesi ve seçiciliği nedeniyle güçlü bir heterojen katalizör olarak özellikle kimyasal sensör uygulamalarında yaygın olarak kullanılmaktadır. Bakır oksit nanopartikülleri sentezlemek için birçok yaklaşım kullanılmaktadır. Bu yöntemlerden sol-jel yöntemi, sıcaklık, reaksiyon süresi, sol çözeltisi pH'ı ve reaktiflerin konsantrasyonu gibi parametrelerin değiştirilmesi ile farklı morfoloji ve boyutta kristalin nanomalzemelerin üretimine olanak sağlamaktır. Çalışmanın amacı sol çözeltisinin pH değeri ve kalsinasyon sıcaklığının sol-jel yöntemiyle sentezlenmiş bakır oksit nanopartiküllerin yapısal ve morfolojik özellikleri üzerindeki etkisini incelemektir. Sentezlenen bakır oksit nanopartiküller, X-ışını kırınımı (XRD), taramalı elektron mikroskobu (SEM), dinamik ışık saçılımı (DLS) ve Fourier dönüşümlü kızılötesi spektroskopisi (FTIR) kullanılarak karakterize edilmiştir. X-ışını kırınımı (XRD) sonuçları sentezlenen nanopartiküllerin safsızlık içermeyen kristal yapıdaki monoklinik bakır oksit yapıda olduğunu ortaya koymuştur. Nanopartiküllerin ortalama kristal boyutu Scherrer formülü kullanılarak hesaplanmış ve 20-30 nm aralığında bulunmuştur. İlave olarak, FTIR spektroskopi analizi de saf bakır oksit nanopartiküllerinin oluşumunu doğrulamıştır. Bulgularımız, incelenen sol-jel proses parametrelerinin sentezlenen bakır oksit nanopartiküllerin yapısal ve morfolojik özellikleri üzerine etkisi olduğunu doğrulamaktadır.

Anahtar Kelimeler: Metal Oksit, CuO, Nanopartikül, Sol-Jel, Kalsinasyon Sıcaklığı, pH Etkisi

1. INTRODUCTION

Oxide-based nanostructures have shown great interest in fundamental and applied research fields due to superior physical, mechanical and chemical properties. Therefore, these materials are becoming widespread as a wide variety of commercial products in many application areas such as electronic and optical devices, cosmetics, catalysts and biosensors. etc.(Bakirhan, Uslu et al. 2017). According to the literature, studies on metal oxide semiconductor materials, such as TiO_2, ZnO, Cu_2O, and CuO, are currently popular because of their wide range of applications in electronic and optoelectronic devices, such as electrochemical cells, gas sensors, magnetic storage devices, field emitters, nano liquids, and catalysts (Kannan, Radhika et al. 2020, Şerban and Enesca 2020, Gautam, Sharma et al. 2021, Soni, Singh et al. 2022). Copper oxide (CuO) is a p-type semiconductor with a narrow band gap value between 1.8 - 2.4 eV at room temperature. CuO is one of the most extensively studied metal oxides because of its low cost, natural abundance and outstanding properties (Jabbar 2016). There are several methods to synthesize CuO nanoparticles, including the sol-gel approach, solid state reaction, sonochemical preparation, alkoxide-based preparation and reflux condensation method. Among them, sol-gel technique is a widely used method for synthesizing nanoparticles due to easy control of process parameters, high product purity and production of homogeneous nanostructures at low temperatures(Milea, Bogatu et al. 2011, Yahaya, Azam et al. 2017, Patel, Mishra et al. 2022). In the sol-gel process, hydrolysis, condensation and polymerisation reactions depend on several parameters and these parameters are highly effective on the structure, morphology and properties of the synthesized nanoparticles (Vahidshad, Abdizadeh et al. 2011). In this context, reagent concentration, catalyst concentration, temperature, mixing mode, rate of hydrolysis, condensation reaction and drying conditions are important parameters that have a significant influence on nanoparticle structural properties (Soytaş, Oğuz et al. 2019). In this study, CuO nanoparticles were synthesized by sol-gel method. Aim of this research is to investigate the effect of pH of the solution and calcination temperatures on structural properties of the synthesized CuO nanoparticles.

2. EXPRIMENTAL STUDY

In order to synthesize CuO nanoparticles by sol-gel process copper acetate dihydrate ($Cu(CH_3COO)2.H_2O$), 2-propanol ($CH_3CH(OH)CH_3$) and monoethanolamine (C_2H_7NO)(EA) (99.5% pure) were used. All chemicals are reagent garde and supplied from Merck. First, copper acetate and isopropyl alcohol were mixed at room temperature for 60 min. After then EA was added drop by drop into solution. The pH of the mixed solution was adjusted to the required level as pH 7, 8 and 9. After mixing step, a homogeneous and transparent solution was obtained. The resulting materials were dried at 80°C overnight. Finally, calcination was performed at varying temperatures (500 and 600 °C) for 1 hour to obtain CuO nanoparticles The structure of the synthesized CuO nanoparticles was studied using X-ray diffraction (XRD, Rigaku, D / Max-2200 / PC). The nanoparticles were analyzed in the range of 2θ from 3 to 90° with a scanning rate of 4° and incidence angle of 1°.The chemical composition of samples examinated by Fourier Transform Infrared Spectroscopy (FTIR) measurements by using Thermo Scientific Nicolet iS50 FT-IR spectrometer in transmission mode. The measurements were performed in a range of 500–4000 cm^{-1} with the resolution of 4 cm^{-1}. Dynamic light scattering analyzes (DLS) were performed to determine the particle size distribution using ZetaSizer Nano ZS90. The morphology of CuO nanoparticles was examined using a scanning electron microscope (LEO EVO-40xVP).

3. RESULT AND DISCUSSION

XRD patterns of the prepared CuO nanoparticles prepared pH values of 7, 8 and 9 are shown in Figure 1. The diffraction patterns depicted that synthesized nanoparticles are composed of monoclinic CuO phase with JCPD card number: 45 – 0937. The peaks at 2θ values 32.48°, 35.52°, 48.72°, 53.45°, 58.33°, 61.54°, 66.23° and 68.05° are assigned to ($\bar{1}10$) , (002), (111), ($\bar{2}02$), (020), (202), ($\bar{1}13$), ($\bar{3}11$) and ($\bar{2}20$) planes of crystalline CuO phase. It can be seen that all samples have phase purity and a defect free lattice according to the XRD patterns of the samples that synthesized at various pH values. The mean crystallite size of CuO nanoparticles was calculated from XRD peak width by using Debye- Scherrer equation (Dorozhkin 2012):

$$D = \frac{k_{Sch}\lambda}{\beta_d cos\theta}$$

where:

D = crystalline size (Å)

k_{Sch} = Scherrer constant and equals to 0.9

λ= X-ray wavelength (1.542 Å)

βd = angular width of half-maximum intensity (degree)

θ= Bragg's angle (degree)

The average crystallite size of CuO nanoparticles were determined to be 21.79, 22.24 and 25.15 for pH values of 7, 8 and 9, respectively. In alkaline conditions, increasing in pH of the solution leads it to generate more OH^- ions, which promotes crystallization and nucleation (Hussen, Dejene et al. 2019). The results revealed that as the pH of the solution rises, the crystallite size of the CuO particles increases. The pH of the precursor solution is strongly influenced by the amount of H^+ or OH^- ions in the initial sol, therefore a change in pH has an impact on the behavior of the solution during the gel formation process in terms of hydrolysis and condensation steps [14].

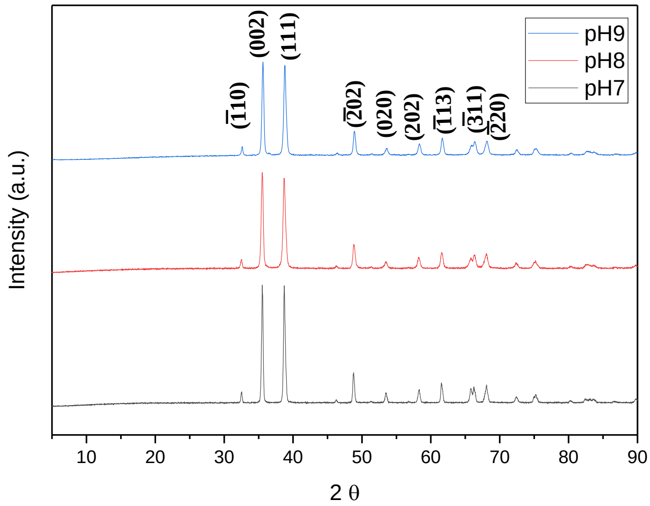
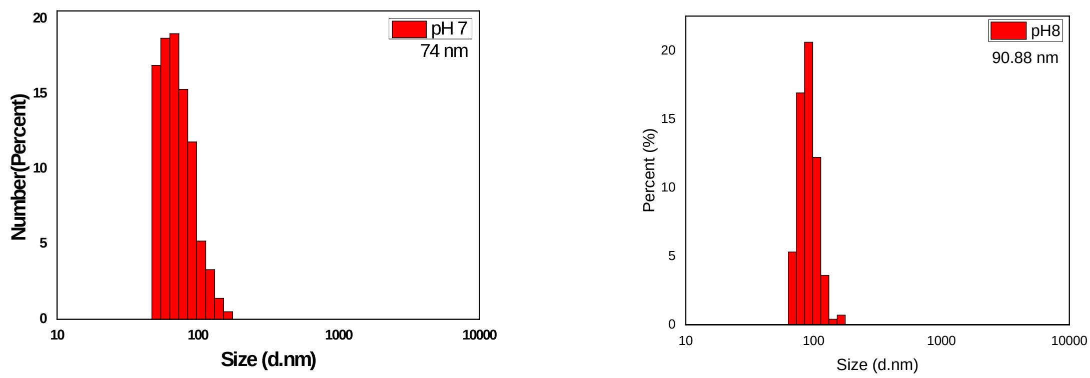


Figure 1. XRD pattern of CuO nanoparticles synthesized at various pH values

DLS method was used to determine the particle size distribution of CuO nanoparticles. Figure 2 shows the crystallite and particle size variations of CuO nanoparticles synthesized at various pH levels. Particle sizes were measured to be 74.90, and 132 nm for pH levels 7, 8, and 9, respectively. The results show that pH of the precursor solution influences the hydrolysis and condensation behavior of the solution during gel formation. Hence, the pH of the solution affects the gel's ability to develop its polymeric three-dimensional structure. The amount of OH^- ions in the solution increases when the pH of the solution is basic, and the alkaline environment promotes the hydrolysis. As a result, an increase in particle size occurs under these conditions. According to the results, OH^- ions, which facilitate CuO nucleation, growth, and particle formation, are responsible for the increase in particle size with increasing pH value. This finding is consistent with the results in the literature, showing an increase in particle size with increasing pH (Sivakumar, Senthil Kumar et al. 2012, Jay Chithra, Sathya et al. 2015, Munir, Munir et al. 2017, Hussen, Dejene et al. 2019).



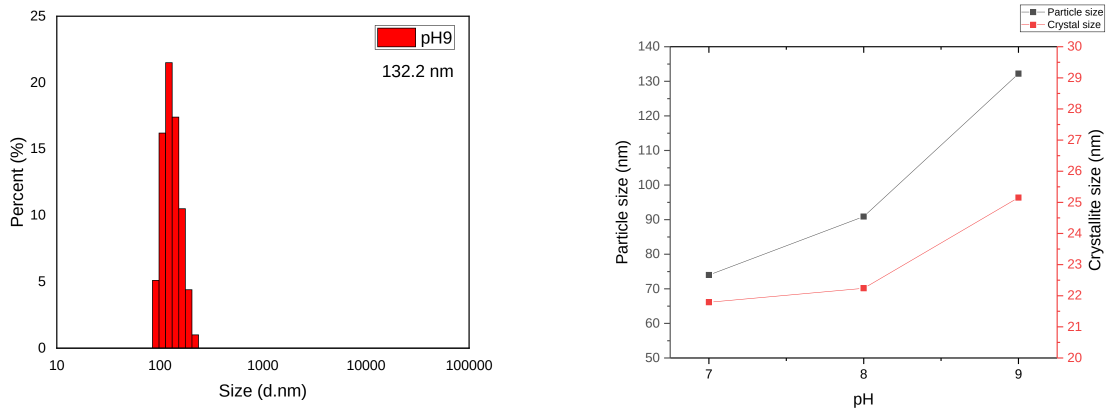


Figure 2. Crystallite and particle size results of CuO nanoparticles synthesized at various pH values.

Fourier transform infrared spectroscopy (FTIR) spectra results of CuO nanoparticles synthesized at various pH values are depicted in Figure 3. The slight vibrations in the range 3600–3800 cm are attributed to O–H stretching vibration (Momeni, Nazari et al. 2014). The vibrations at 1400-2200 cm^{-1} are caused by the humidity in the air and CO_2 (NAKTİYOK and ÖZER , Singh, Kumar et al. 2016). The adsorption at 537 cm^{-1} are the characteristic stretching vibrations of Cu-O bond in monocilinic CuO(Attou, Jaber et al. 2018, Sahu, Raj et al. 2021). The FTIR results are also in good agreement with the XRD analysis results.

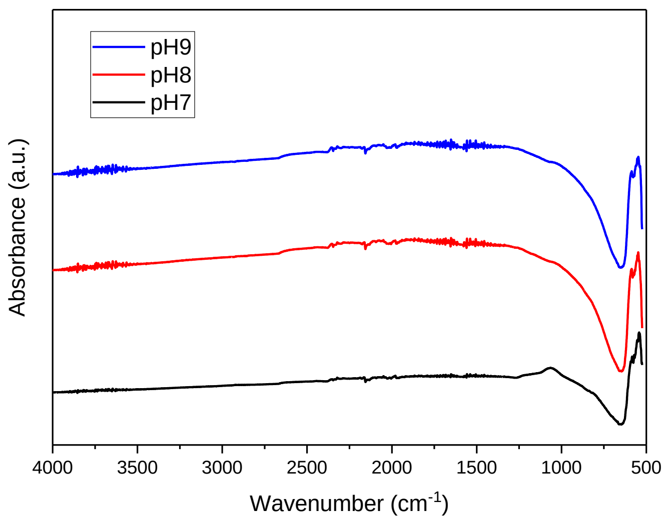


Figure 3. FTIR spectra of CuO nanoparticles synhesized at various pH values.

The calcination temperature has an effect on the structural properties such as particle size, crystallinity and phase structure of the particles obtained by the sol-gel method (Ibrahim and Sreekantan 2011). As a result, the materials' structural characteristics and microstructures could be controlled by changing the calcination temperature. According to our findings regarding size measurement, it was determined that CuO nanostructures with the smallest particle size were synthesized at pH 7. Therefore, the effect of calcination temperature on the structural properties of CuO nanoparticles synthesized at pH 7 was investigated. Figure 4 depicts the XRD patterns of synthesized CuO nanoparticles calcinated at 500 °C and 600 °C. The XRD patterns shows two sharp peaks around 2θ = 35.5° and 38°, corresponding to the (002) and (111) plane reflections, respectively. Obtained XRD pattern is attributed to the presence of monoclinic CuO crystal phase (JCPD card number: 45 – 0937). Moreover, no characteristic peaks assigned to impurities or minor phase were detected. It can be seen that that as the calcination temperature rises, the XRD peak density increases while the peak width decreases.

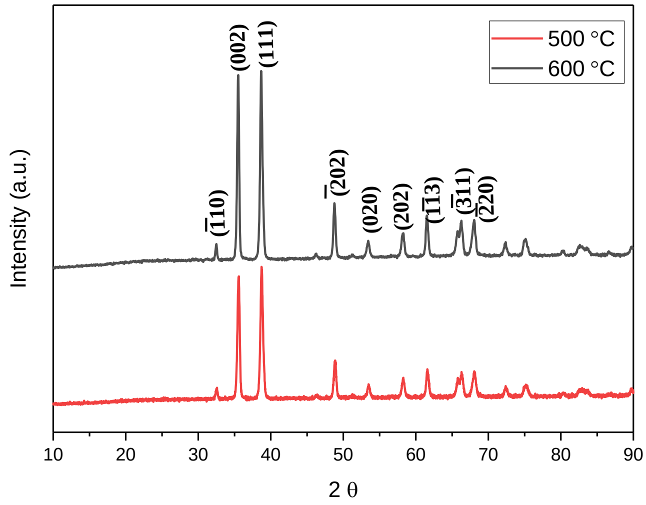


Figure 4. XRD patterns of CuO nanoparticles synthesized at different calcination temperatures

Figure 5 shows the DLS measurement results of copper oxide nanostructures. The average particle and crystallite size of the copper oxide nanoparticles increase as the calcination temperature increases due to high agglomeration. The average crystallite size of CuO nanoparticles calculated using the Debye Scherer formula is approximately 21.79 nm and 25.63 nm for calcination temperatures of 500 and 600C, respectively.The results of the particle size analysis showed that the particle size of CuO nanostructures increased from 74 nm to 238 nm as the calcination temperature was increased from 500°C to 600°C. It was found that the thermally induced crystallite growth with increasing calcination temperature results in an increase in crystallite size.(Phromma, Wutikhun et al. 2020). Therefore, it was concluded that increasing calcination temperature leads to an increase in crystallite size of the CuO particles.

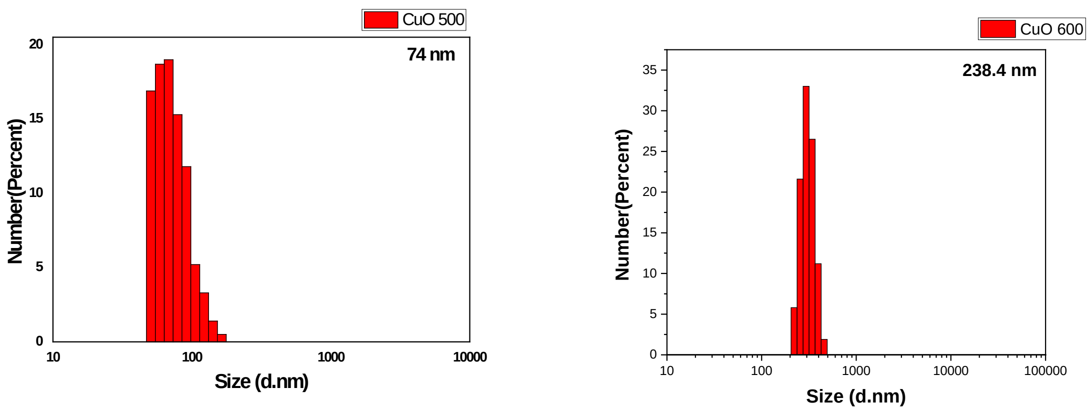


Figure 5. Particle size distribution of CuO nanoparticles calcinated at different temperatures.

Figure 6 demonstrates the FTIR spectra of CuO nanoparticles calcinated at different temperatures. It can be noticed that the band vibrations of the resulting spectrum are similar to those of the spectrum obtained from study on the pH effect. The broad band around 3600 cm-1 assigned to O-H stretching mode of hydroxyl group [17]. The band in the range of 1400 to 2200 cm-1 are caused by the humidity in the air and CO2 [18, 19]. The adsorption band observed at 537 cm−1 are due to stretching vibrations of CuO [20, 21]. This result indicates the success in producing CuO nanoparticles.

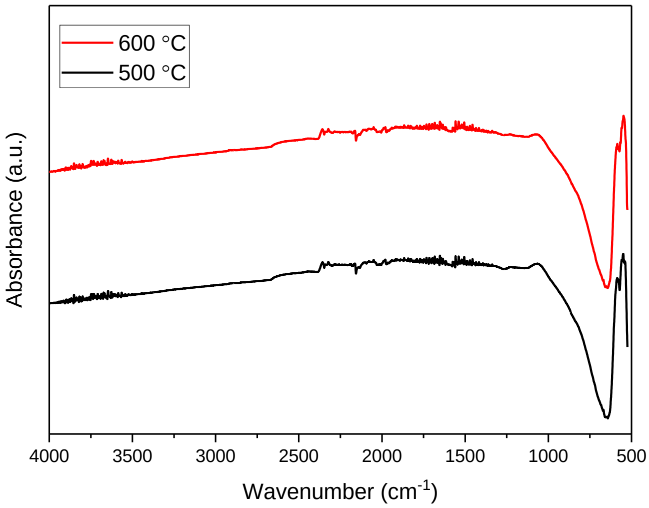


Figure 6. FTIR spectra of CuO nanoparticles calcined at different temperatures.

The SEM image given in Figure 7 shows the morphology CuO nanoparticles obtained under the conditions of a pH 7 solution and a calcination temperature of 500 °C. It shows a distribution of spherical particles of the prepared CuO nanoparticles with the diameter approximately 74 nm. As can be seen from the SEM image, the CuO particle size measurement results were found to be in good accordance with the data of the DLS analyses.

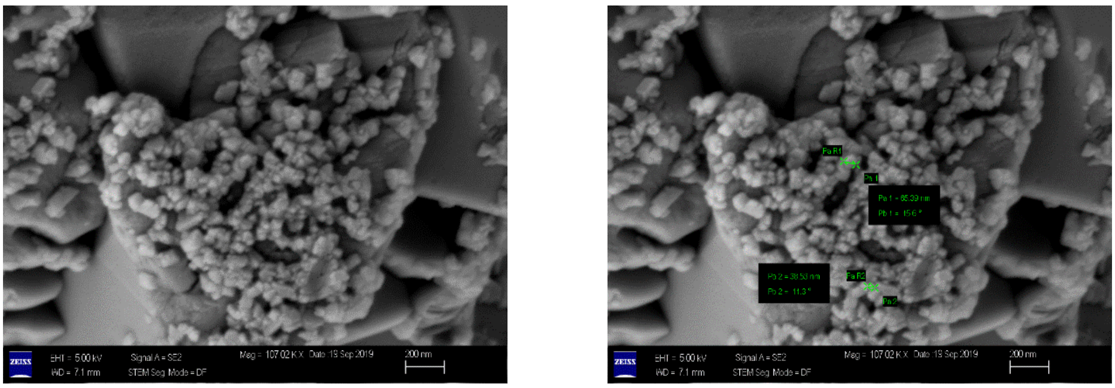


Figure 7. SEM image of CuO nanoparticles-pH 7 calcinated at 500 °C.

4. CONCLUSIONS

In this paper we have reported the results of CuO nanoparticles synthesized by sol-gel method at various calcination temperatures and pH levels. The synthesized CuO nanoparticles were characterized by XRD, DLS, FTIR and SEM analysis. CuO structure synthesized at 500 °C has good structural and morphological properties. It was found that all of the CuO structures synthesized by altering the pH value of the solution were successfully produced at the crystal structure and nanoscales. The crystallite and particle size of the synthesized nanoparticles increased with an increase in pH value of the precursor solution. It was concluded that the increase in the calcination temperature led to a significant increase in the size of the nanoparticles. The obtained results demonstrated that CuO nanostructure structural characteristics may be controlled by modifying the calcination temperature and solution pH value.

REFERENCES

Attou, L., B. Jaber and H. Ez-Zahraouy (2018). "Effect of annealing temperature on structural, optical and photocatalytic properties of CuO nanoparticles." Mediterranean Journal of Chemistry 7(5): 308-316.

Bakirhan, N. K., B. Uslu and S. A. Ozkan (2017). Sensitive and selective assay of antimicrobials on nanostructured materials by electrochemical techniques. Nanostructures for Antimicrobial Therapy, Elsevier: 55-83.

Dorozhkin, S. V. (2012). "Calcium orthophosphate coatings, films and layers." Progress in Biomaterials 1(1): 1.

Gautam, Y. K., K. Sharma, S. Tyagi, A. K. Ambedkar, M. Chaudhary and B. Pal Singh (2021). "Nanostructured metal oxide semiconductor-based sensors for greenhouse gas detection: Progress and challenges." Royal Society open science 8(3): 201324.

Hussen, M. K., F. B. Dejene and M. Tsega (2019). "Effect of pH on material properties of ZnAl2O4: Cr3+ nano particles prepared by sol–gel method." Journal of Materials Science: Materials in Electronics 30(11): 10191-10201.

Ibrahim, S. A. and S. Sreekantan (2011). Effect of pH on TiO2 nanoparticles via sol-gel method. Advanced Materials Research, Trans Tech Publ.

Jabbar, S. M. (2016). "Synthesis of CuO nano structure via sol-gel and precipitation chemical methods." Al-Khwarizmi Engineering Journal 12(4): 126-131.

Jay Chithra, M., M. Sathya and K. Pushpanathan (2015). "Effect of pH on crystal size and photoluminescence property of ZnO nanoparticles prepared by chemical precipitation method." Acta Metallurgica Sinica (English Letters) 28(3): 394-404.

Kannan, K., D. Radhika, A. Nesaraj, K. K. Sadasivuni, K. R. Reddy, D. Kasai and A. V. Raghu (2020). "Photocatalytic, antibacterial and electrochemical properties of novel rare earth metal oxides-based nanohybrids." Materials Science for Energy Technologies 3: 853-861.

Milea, C., C. Bogatu and A. Duta (2011). "The influence of parameters in silica sol-gel process." Bulletin of the Transilvania University of Brasov. Engineering Sciences. Series I 4(1): 59.

Momeni, M., Z. Nazari, A. Kazempour, M. Hakimiyan and S. Mirhoseini (2014). "Preparation of CuO nanostructures coating on copper as supercapacitor materials." surface engineering 30(11): 775-778.

Munir, T., H. Munir, M. Kashif, M. FAKHAR-E-ALAM, A. Shahzad, N. Amin, A. Sajid and M. Umair (2017). "Synthesis and characterization of Copper Oxide nanoparticles by solution evaporation method." Journal of Optoelectronics and Advanced Materials 19(May-June 2017): 417-423.

NAKTİYOK, J. and A. K. ÖZER "Synthesis Of Copper Oxide (Cuo) From Thermal Decomposition Of Copper Acetate Monohydrate (Cu (CH3COO) 2. H2O)." Niğde Ömer Halisdemir Üniversitesi Mühendislik Bilimleri Dergisi 8(2): 1292-1298.

Patel, M., S. Mishra, R. Verma and D. Shikha (2022). "Synthesis of ZnO and CuO nanoparticles via Sol gel method and Its Characterization by using XRD and FT-IR Analysis."

Phromma, S., T. Wutikhun, P. Kasamechonchung, T. Eksangsri and C. Sapcharoenkun (2020). "Effect of calcination temperature on photocatalytic activity of synthesized TiO2 nanoparticles via wet ball milling sol-gel method." Applied Sciences 10(3): 993.

Sahu, K. K., B. Raj, S. Basu and M. Mohapatra (2021). "Calcination Strategy for Scalable Synthesis of Pithecellobium-Type Hierarchical Dual-Phase Nanostructured Cu x O to Columnar Self-Assembled CuO and Its Electrochemical Performances." ACS omega 6(2): 1108-1118.

Singh, P. K., P. Kumar, M. Hussain, A. K. Das and G. C. Nayak (2016). "Synthesis and characterization of CuO nanoparticles using strong base electrolyte through electrochemical discharge process." Bulletin of Materials Science 39(2): 469-478.

Sivakumar, K., V. Senthil Kumar, N. Muthukumarasamy, M. Thambidurai and T. Senthil (2012). "Influence of pH on ZnO nanocrystalline thin films prepared by sol–gel dip coating method." Bulletin of Materials Science 35(3): 327-331.

Soni, V., P. Singh, A. A. P. Khan, A. Singh, A. K. Nadda, C. M. Hussain, Q. Van Le, S. Rizevsky, V.-H. Nguyen and P. Raizada (2022). "Photocatalytic transition-metal-oxides-based p–n heterojunction materials: synthesis, sustainable energy and environmental applications, and perspectives." Journal of Nanostructure in Chemistry: 1-38.

Soytaş, S. H., O. Oğuz and Y. Z. Menceloğlu (2019). Polymer nanocomposites with decorated metal oxides. Polymer Composites with Functionalized Nanoparticles, Elsevier: 287-323.

Şerban, I. and A. Enesca (2020). "Metal oxides-based semiconductors for biosensors applications." Frontiers in Chemistry 8: 354.

Vahidshad, Y., H. Abdizadeh, H. Baharvandi and M. Akbari Baseri (2011). "Sol-Gel synthesis and characterization of copper stabilized zirconia nanoparticles." International Journal of Modern Physics B 25(21): 2823-2839.

Yahaya, M. Z., M. A. Azam, M. A. M. Teridi, P. K. Singh and A. A. Mohamad (2017). "Recent characterisation of sol-gel synthesised TiO2 nanoparticles." Recent applications in Sol-Gel synthesis: 109-129.