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Structural and morphological properties of copper oxide nanoparticles using precipitation-thermal oxidation method

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Abstract

In this study, copper oxide (CuO) nanoparticles were produced using the precipitation thermal oxidation method. Two parameters were studied: heating time and sintering temperature. To investigate the surface structure and crystallinity of the samples, field emission scanning electron microscopy (FESEM) and x-ray diffraction (XRD) were used. The effect of heating time on the production of nanoparticles was investigated. Heating time of 1 hour, 3 hours and 5 hours were conducted. The amount of CuO formed was affected by heating times, with the formation of nanoparticles seen after 3 hours of heating. The CuO nanoparticles produced uniformly as the heating time increased. During the nanoparticles production, the heating temperature remained constant at 110 °C throughout the heating time. Furthermore, CuO nanoparticles are produced at different sintering temperatures of 300 °C and 400 °C in order to study the influence of temperature on the size of the nanoparticles. At 300 °C of sintering temperature, the formation of CuO nanoparticles was formed with more uniform structure. According to the findings of this study, both parameters have an impact on the production of CuO nanoparticles.

Keywords: Copper oxide, precipitation process, nanoparticles, growth formation

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1. Introduction

The great interest in nanomaterials has prompted the study and investigation for various nanostructures especially nanoparticles. Nanoparticles have applications in diverse fields including catalysis, energy conversion, storage, environmental and sensing devices which depends on the control of its size and shape of the materials [1]. Metal oxide nanoparticles often demonstrate their specific properties opposed to their corresponding bulk materials which give rise to distinctive quantum properties. Copper oxide (CuO) have drawn attention due to their unique chemical and physical properties finding applications in many areas including catalysis [2], energy conversion and storage [3], antimicrobial agents [4], optoelectronic devices [5], and sensors [6]. Notably, copper oxides comprise of two stable forms, CuO and Cu_2O which is a direct bandgap semiconductor with the bandgap values in the range 1.3–1.7 eV and 2.0–2.5 eV, respectively [7].

To date various methods have been developed to synthesize CuO nanoparticles such as sol-gel method [8], hydrothermal method [9], co-precipitation method [10] and microwave assisted methods [11]. The synthesize method mentioned above indeed are easy and reliable, however this method typically encounters potential problems such as the growth proceeds at high temperature and requires costly experimental setups [12]. Therefore, the suitable and facile fabrication of copper oxide nanoparticles approach is through precipitation thermal oxidation method which is simple reaction process with affordable reaction parameters.

2. Materials and methods

2.1. Synthesis of CuO nanoparticles

The method to synthesize CuO nanoparticles was inspired by Jiang et al. (2018), using simple precipitation thermal oxidation. Briefly, 2.0 g of cupric acetate, 5 mL of water, and 45 mL of ethylene glycol transferred into the conical flask. The mixture was heated and stirred for 5 hours at 110 °C. The formed precipitates then were filtered and heated for 2 hours at 80 °C. Subsequently, the precipitate was thermally treated for 1 hours at temperature 300 °C.

2.2. Characterization

The crystallinity and phase transition were identified by an x-ray diffractometer (XRD) under powder scanning mode with the X-ray source of Cu-K_α radiation

that emitted a wavelength of 0.154 nm. The morphology of CuO nanoparticles were observed using field emission scanning electron microscope (FESEM).

3. Results and discussion

3.1. Structural Properties

The structural properties and crystallinity identification of CuO nanoparticles were observed by XRD patterns as in Fig. 1 for different heating time of 1 hour, 3 hours and 5 hours. Diffraction sharp peaks at 2θ values of 32.78°, 35.86°, 39.21°, 49.26°, 54.01°, 61.83°, 66.58°, 68.39°, 72.86° and 75.51° were assigned to (1 1 0), (0 0 2), (1 1 1), (2 0 2), (0 2 0), (− 1 1 3), (− 3 11), (2 2 0), (3 1 1) and (− 2 2 2) which correspond to the monoclinic structure of CuO [13]. With the broadening of diffraction peaks, the crystallite size of the sample can be approximately calculated using Debye-Scherrer's equation [14]. The average crystallite size was about 16.74 nm. The peaks broadening inferring such that smaller particle size formed with increasing heating time from 1 hour to 5 hours, demonstrating an increment in the average crystallite size and hence crystallinity of the CuO nanoparticles [15].

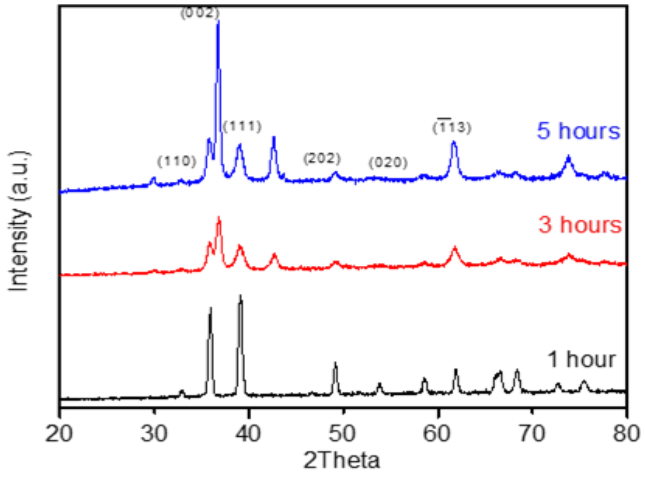

Fig. 1 XRD pattern of CuO heated at different heating time at 1 hour, 3 hours and 5 hours, respectively

The XRD patterns of CuO nanoparticles at different sintering temperatures from 300 °C to 400 °C are shown in Fig. 2. The diffraction peaks for different sintering temperature were indexed to (1 1 0), (0 0 2), (1 1 1), (2 0 2), (0 2 0), and (− 1 1 3) which consistent to monoclinic phase of CuO. From the plot, it is observed that increased in peak intensity with respect to the sintering temperature. This indicates that with higher peak intensity, degree of crystallinity is increased. With the increase of sintering temperature, peak narrowing is observed due to the removal of grain boundaries, thus improved its crystallinity [16].

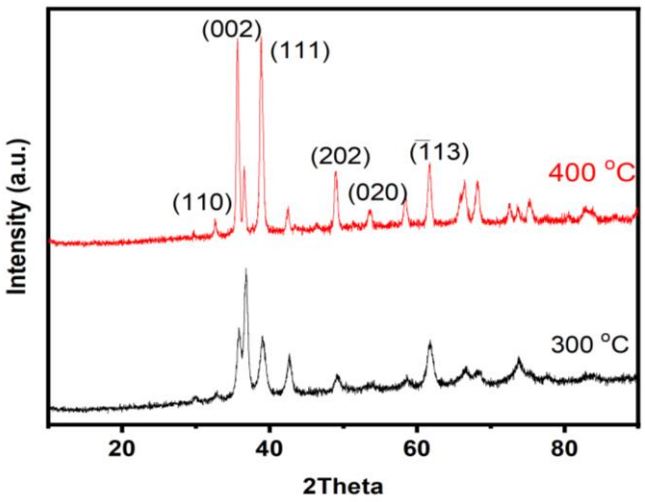

Fig. 2 XRD pattern of CuO sintered 1 hour at different temperature for 300 °C and 400 °C, respectively

3.2. Morphological properties

3.2.1 The effect of heating time

The morphology of CuO nanostructures was investigated at different heating time using FESEM micrograph as seen in Fig. 3. Formation of precipitate was observed post 1 hour of heating. The nanoparticles have started to form though its structural is not evenly distributed which is possibly due to the short nucleation time. As the heating time increase to 3 hours, a distinct formation of CuO nanoparticles with a relatively uniform structure was discovered with diameter 60.79 nm and 62.55 nm at two different spots as indicate in Fig. 3(b). As the nucleation time for formation of nanoparticle is longer, its structure is perceived with a well distribution size of the nanoparticle with a small agglomeration of particle. The CuO nanoparticles synthesized for heating time of 3 hours appear much less densely clustered [17]. Regardless, after heating at 5 hours, the structure of the nanoparticles is unsustainable which do not correspond with the literature where the formation of the nanoparticles should be uniformly formed at 5 hours of heating time [18]. At 5 hours not only were there extensive agglomeration to larger particle but there was also coalescence of the nanoparticles which could be observed. The agglomerated nanoparticles were attached with each other randomly, forming compact CuO nanostructure. Therefore, the longer heating time enhanced agglomeration of nanoparticles.

3.2.2 The effect of sintering temperature

The morphology of CuO nanoparticles at different sintering temperature of 300 °C and 400 °C is displayed in FESEM micrograph in Fig. 4. At 300 °C, CuO nanoparticle structure was constructed uniformly. The structures reveal an increase in particles size initially with increase in sintering temperature. However, upon sintering at 400 °C, formation of nanoparticle is indistinguishable which can be observed in Fig. 4(b) as it demonstrates a compact

aggregation structure. CuO nanoparticles were agglomerated due to supersaturation condition. The tendency to agglomerate is due to the rising nucleation and growth rates resulting from a higher thermal energy with the increased of sintering temperature from 300 °C to 400 °C. The crystallite size tends to grow more rapidly when heated up to higher temperatures. A significant narrow size distribution of the nanoparticles leads to higher surface area. Increase of temperature not only accelerates nucleation rate but also enhances particle growth. From the micrographs clearly showed that the particles were roughly agglomerated with homogeneous morphologies due to oxidation of metal nanoparticles [19].

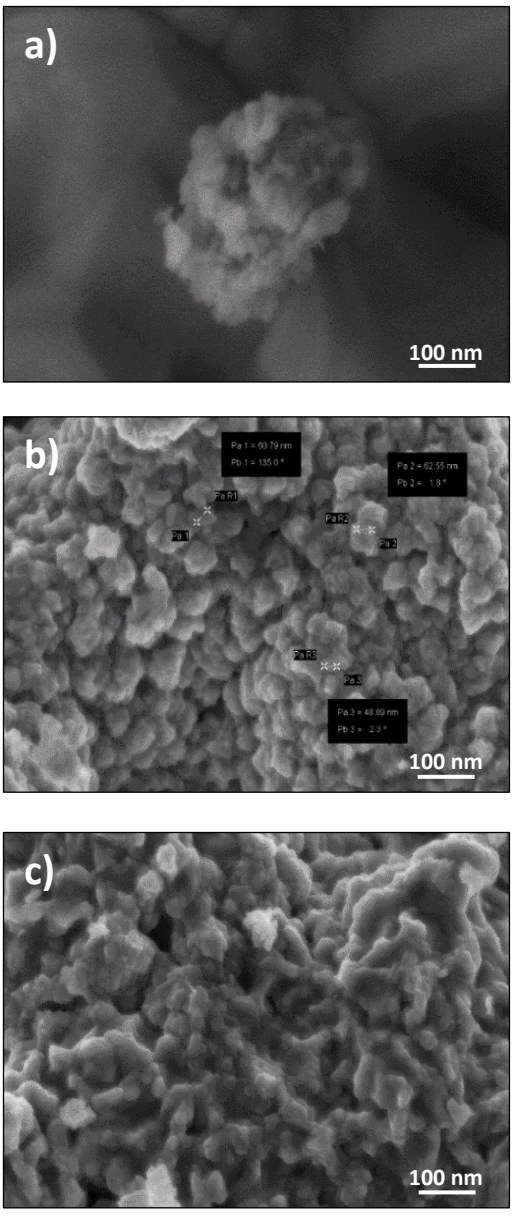

Fig. 3. The micrograph of CuO NPs obtained by FESEM at different heating time (a) 1 hour, (b) 3 hour and (c) 5 hours

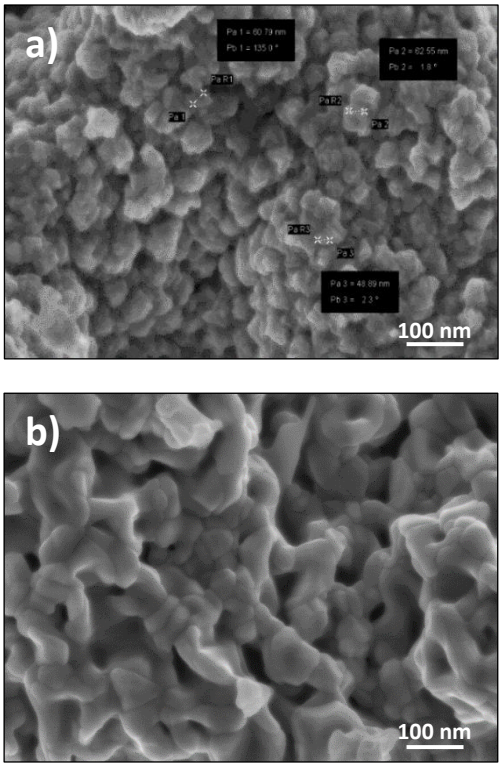

Fig. 4. The micrograph of CuO NPs obtained by FESEM at different sintering temperature (a) 300 °C (b) 400 °C

4. Conclusions

In this study, CuO nanoparticles were formed using a precipitation thermal oxidation method, with the heating time and sintering temperature being changed to see how they affected the nanoparticles production. The nanoparticles were successfully synthesized using different heating times of 1 hour, 3 hours and 5 hours. Apart from the size of the nanoparticles, the quantity of CuO was affected by varied heating times. In addition, changing in sintering temperature have affected the structure and size of the nanoparticles, as well as their properties. CuO sintered at 300 °C shows the best nanoparticles structure compare to 400 °C. It was discovered that the shape of CuO nanoparticles differed depending on the sintering temperature. At 400 °C, the size distribution of the nanoparticles was not uniform in size that led to agglomeration. This is because sintering temperature has affected the growth of the nanostructure where the sintering temperature can control the growth of CuO nanoparticles.

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References

[1] M.B. Gawande, A. Goswami, F.-X. Felpin, T. Asefa, X. Huang, R. Silva, X. Zou, R. Zboril and R.S. Varma. (2016). Cu and Cu-based nanoparticles: synthesis and applications in catalysis. Chemical Reviews. 116(6): 3722-3811.

[2] R. Nayak, F.A. Ali, D.K. Mishra, D. Ray, V.K. Aswal, S.K. Sahoo and B. Nanda. (2020). Fabrication of CuO nanoparticle: An efficient catalyst utilized for sensing and degradation of phenol. Journal of Materials Research and Technology. 9(5): 11045-11059.

[3] A.C. Nwanya, M.M. Ndipingwi, C.O. Ikpo, R. Obodo, S.C. Nwanya, S. Botha, F.I. Ezema, E.I. Iwuoha and M. Maaza. (2020). Zea mays lea silk extract mediated synthesis of nickel oxide nanoparticles as positive electrode material for asymmetric supercabattery. Journal of Alloys and Compounds. 822: 153581.

[4] A. George, D.M.A. Raj, A.D. Raj, A.A. Irudayaraj, J. Arumugam, H.J. Prabu, S.J. Sundaram, N.A. Al-Dhabi, M.V. Arasu and M. Maaza. (2020). Temperature effect on CuO nanoparticles: Antimicrobial activity towards bacterial strains. Surfaces and Interfaces. 21: 100761.

[5] M.A. Khan, N. Nayan, M.K. Ahmad, S.C. Fhong, M.S.M. Ali, M.K. Mustafa and M. Tahir. (2021). Interface study of hybrid CuO nanoparticles embedded ZnO nanowires hetero-junction synthesized by controlled vapor deposition approach for optoelectronic devices. Optical Materials. 117: 111132.

[6] K. Kaviyarasu, G.T. Mola, S.O. Oseni, K. Kanimozhi, C.M. Magdalane, J. Kennedy and M. Maaza. (2019). ZnO doped single wall carbon nanotube as an active medium for gas sensor and solar absorber. Journal of Materials Science: Materials in Electronics. 30(1): 147-158.

[7] D. Gupta, S.R. Meher, N. Illyaskutty and Z.C. Alex. (2018). Facile synthesis of Cu_2O and CuO nanoparticles and study of their structural, optical and electronic properties. Journal of Alloys and Compounds. 743: 737-745.

[8] J. Jayaprakash, N. Srinivasan, P. Chandrasekaran and E.K. Girija. (2015). Synthesis and characterization of cluster of grapes like pure and zinc-doped CuO nanoparticles by sol-gel method. Spectrochimica Acta Part a-Molecular and Biomolecular Spectroscopy. 136: 1803-1806.

[9] R. Jana, A. Dey, M. Das, J. Datta, P. Das and P.P. Ray. (2018). Improving performance of device made up of CuO nanoparticles synthesized by hydrothermal over the reflux method. Applied Surface Science. 452: 155-164.

[10] M. Karimi, S.A. Hassanzadeh-Tabrizi and A. Saffar-Teluri. (2017). In situ reverse co-precipitation synthesis and magnetic properties of $CuO/CuFe_2O_4$ nanocomposite. Journal of Sol-Gel Science and Technology. 83(1): 124-131.

[11] A.V. Nikam and A.H. Dadwal. (2019). Scalable microwave-assisted continuous flow synthesis of CuO nanoparticles and their thermal conductivity applications as nanofluids. Advanced Powder Technology. 30(1): 13-17.

[12] D. Mattia. (2015). Hierarchical 3D ZnO nanowire structures via fast anodization of zinc. Journal of Materials Chemistry A View. 3: 17569-17577.

[13] H. Veisi, B. Karmakar, T. Tamoradi, S. Hemmati, M. Hekmati and M. Hamelian. (2021). Biosynthesis of CuO nanoparticles using aqueous extract of herbal tea (*Stachys Lavandulifolia*) flowers and evaluation of its catalytic activity. Scientific Reports. 11(1): 1983.

[14] V. Sudha, G. Murugadoss and R. Thangamuthu. (2021). Structural and morphological tuning of Cu-based metal oxide nanoparticles by a facile chemical method and highly electrochemical sensing of sulphite. Scientific Reports. 11(1): 3413.

[15] M. Verma, V. Kumar and A. Katoch. (2018). Sputtering based synthesis of CuO nanoparticles and their structural, thermal and optical studies. Materials Science in Semiconductor Processing. 76: 55-60.

[16] M. Shaheen, N.H. Kalwar, A. Intisar, Z. Batool, S. Rasheed and R. Kousar. (2021). Efficient surfactant modified copper oxide nanoparticles for solar light driven water purification. Optical Materials. 122: 111688.

[17] L. Dörner, C. Cancellieri, B. Rheingans, M. Walter, R. Kägi, P. Schmutz, M.V. Kovalenko and L.P. Jeurgens. (2019). Cost-effective sol-gel synthesis of porous CuO nanoparticle aggregates with tunable specific surface area. Scientific Reports. 9(1): 1-13.

[18] T. Jiang, M. Bujoli-Doeuff, E. Gautron, Y. Farré, L. Cario, Y. Pellegrin, M. Boujtita, F. Odobel and S. Jobic. (2018). Cu_2O@ CuO core-shell nanoparticles as photocathode for p-type dye sensitized solar cell. Journal of Alloys and Compounds. 769: 605-610.

[19] M. Ramzan, R.M. Obodo, S. Mukhtar, S. Ilyas, F. Aziz and N. Thovhogi. (2021). Green synthesis of copper oxide nanoparticles using *Cedrus deodara* aqueous extract for antibacterial activity. Materials Today: Proceedings. 36: 576-581.