JOURNAL OF MODERN MANUFACTURING SYSTEMS AND TECHNOLOGY (JMMST)
e-ISSN: 2636-9575
VOL. 5, ISSUE 1, 18 – 22
DOI: https://doi.org/10.15282/jmmst.v5i1.5891

ORIGINAL ARTICLE

Morphological changes of ZnO nanostructures upon addition of Trisodium Citrate ($Na_3C_6H_5O_7$) at different reaction temperatures

Aqilah Kamaruzaman*, Nurul Akmal Che Lah

Innovative Manufacturing, Mechatronics, Sports (Imams) Lab, Faculty of Manufacturing Mechatronics Engineering Technology, Universiti Malaysia Pahang, 26600, Pekan, Pahang, Malaysia

ABSTRACT – Due to its interesting physical and chemical properties, zinc oxide (ZnO) is considered one of the front runners of numerous metal oxide semiconductors. In this paper, ZnO nanostructure are synthesised by hydrothermal method with trisodium citrate (TC) as the emulsfying agent. The mean diameetr of ZnO nanostructure are observed with increment of reaction temperature. The mean size results into no change to mean diameter upon increment of reaction temperature but the cumulative frequencies of size distribution showing ZnO nanostructure synthesised in higher temperature to have narrower size distribution. The addition of TC also results into much smaller ZnO nanostructure with mean diameter 8nm

ARTICLE HISTORY
Revised: 19th February 2021
Accepted: 19th February 2021

KEYWORDS
Zinc Oxide; Tannic acid; green synthesis; hydrothermal method; TEM

INTRODUCTION

As one of the most significant metal oxide nanoparticles, zinc oxide is commonly used in different fields due to their unique physical and chemical properties[1, 2]. It optical characteristic of having wide bandgap (3.2-3.7 eV) with strong binding energy (60meV) was a plus point for developing optoelectronic and nanoelectronic application devices [3, 4]. Broad band gap character evolution can be affected by the small size of the ZnO nanostructures (average diameter < 100nm). Zinc oxide can also be used in other industries, including concrete processing, photocatalysis, electronics industries [5]. The biocompatible ability of ZnO nanostructures that can be used together to inhibit microbial growth has been established in a few reported studies [6-10]. Besides, due to their wide surface area and high catalytic activity, ZnO nanostructures have a great advantage of being added to a catalytic reaction phase [11]. Since zinc oxide has various physical and chemical properties depending on the morphology of nanostructures, it is important to investigate not only different methods of synthesis but also the physical and chemical properties of synthesized zinc oxide in terms of its morphology.

Many methods had been described in synthesising ZnO nanoparticles such as wet chemical, hydrothermal, sol-gel and green synthesis method [12-16]. Herein, the hydrothermal process with emulsifying agent Sodium Tricitrate (ST) was used for the synthesis of ZnO nanostructure. The hydrothermal method is well known for it direct method with cost-effective and ecologically advantageous in synthesising nanomaterials [17-20]. The creation of ZnO particles exploited the effect of trisodium citrate on the shape and size of the crystal used as a capping agent [21]. The citrate ions from TS strongly interacted with metal ions and significantly altered the crystal morphology [22].

This study aimed to synthesise smaller size (average diameter < 20 nm) of ZnO nanostructures with the aid of ST as both the structure influencer and capping agent. As the size of ZnO Nanostructures obtained is smaller, the surface area would widen which influenced to the better the optical character of the nanostructures.

MATERIALS AND CHARACTERISATION

Materials: All materials were purchased from the commercial market with high purity (95%) and used without further purification. Zinc powder (Zn) as the starting materials, Trisodium Citrate ($Na_3C_6H_5O_7$) as a capping agent and distilled water as dispersing solvent were used to prepare ZnO nanoparticle.

*CORRESPONDING AUTHOR | A. Kamaruzaman | ✉ aqilah996@gmail.com

Preparation of ZnO nanoparticles: 0.4g of ZnO powder and 0.2g Trisodium CIntrate (TC) powder is diluted in 100ml of distilled water in a beaker. The mixture is then placed on a heated plate and stirred continuously with a heated temperature of 90˚C for 1 hour and 30 minutes. Upon the process, the beaker is then left cooled in the open air, which helps in terminating the regrowth of ZnO nanostructure. The mixture of the pure ZnO solution is then rinse with distilled water and centrifuged to evacuate other impurities. The process of rinsing and centrifuging are repeated for three times. The step is then repeated with two other reaction temperature of 70 and 50°C. Details summary of sample preparation are as shown in **Table 1.**

Table 1: Summary of the parameters used in the preparation of each sample

Sample	Volume of solvent (ml)	Mass of ZnO (g)	Mass of TC (g)	Reaction Temperature (°C)
1	100	0.4	-	90
2	100	0.4	0.1	70
3	100	0.4	0.4	50

Characterisation methods: The morphological structure of the synthesised ZnO and ZnO-TA nanostructures is characterised by the transmission electron microscope (TEM) to monitor the nanostructures' size where 8 to 10 ml of concentrated ZnO Nanostructure are diluted with distilled water. The solution is vigorously shaken and poured into the sample vial. The sample vial is then undergo sonication in the sonicated bath. After about 20 minutes of sonication, the sample is ready for TEM analysis. A drop of sample is drop onto Au (gold) substrate. The samplea are leave to dry for 24 hours before placing into blank microscope slide. The sample are ready to be observe under TEM. The size of the sample are measured by using Gatan Micrsoscopic Suite Software whicha are directly used after monitoring on to the sample at TEM.

RESULT AND DISCUSSION

Morphological Structure

The TEM images of as- synthesised ZnO nanostructure at the temperature of 90, 70 and 50°C are as shown in **Figure 1, 2 and 3** respectively. The size distribution is plotted from the figure, which can be observed that the ZnO nanostructure has a tiny size with an average diameter of 8 nm for the nanostructure synthesised in different temperatures, respectively. As noticed, as the synthesised temperature increased, the cumulative frequencies of the ZnO nanostructure showing steeper gradient, which indicates the presence of narrower size distribution of nanostructure. Thus, we can observe that the range size for ZnO nanostructure synthesised at 70 and 90°C are generally smaller than the nanostructure synthesised at 50°C. This is believe happened due to aggregation that occurred. The presence of ST generally enhanced resulting in really small diameter of the ZnO nanostructure.

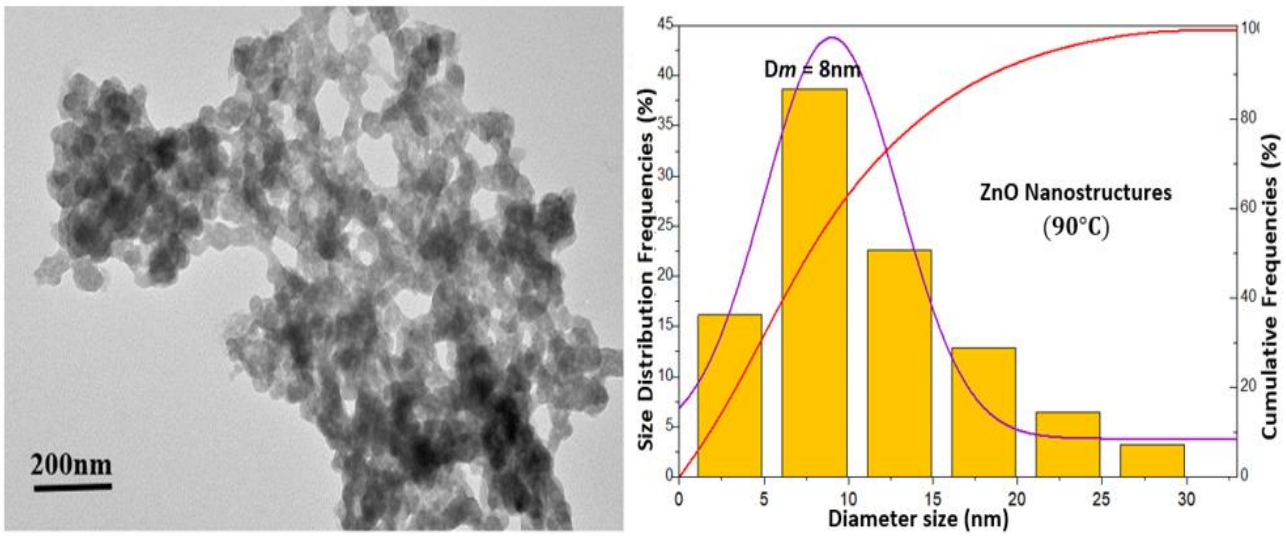

Figure 1: TEM image and size distribution chart of synthesised ZnO nanostructure synthesised at temperature **90**°C.

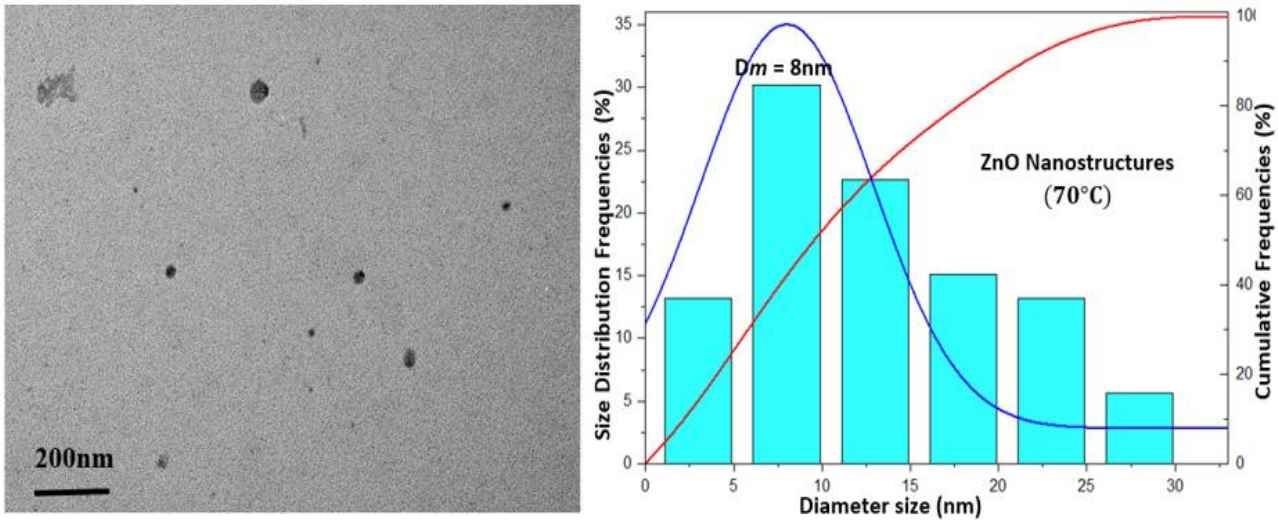

Figure 2: TEM image and size distribution chart of synthesised ZnO nanostructure synthesised at temperature **70**°C.

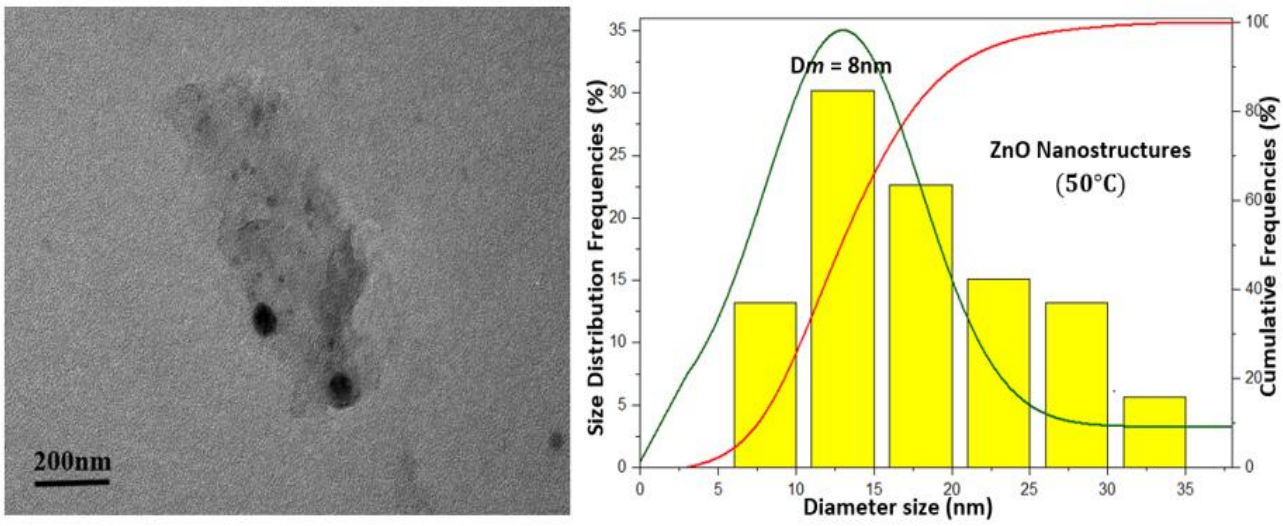

Figure 3: TEM image and size distribution chart of synthesised ZnO nanostructure synthesised at temperature **50**°C.

As the reaction temperature is higher, the ionization and deposition rate take place faster. Thus, this result in the size of particle synthesised to be narrower [23]. Besides, the ZnO nanostructure synthesised in higher temperature also results in a high density of ionization oxygen deficiencies which will enhance the optical character of the nanoparticle [24]. Whilst, the TC added serves as a surfactant which allows the solvent's surface tension to be quickly dispersed and reduced. Further, it also serves as a reaction hosting microreactor and a steric stabilizer to prevent aggregation [25, 26]. The interaction of $Na_3C_6H_5O_7$ with ZnO growing species suppressed the growth process and reduced crystallite size. As more citrate ions were present in the precursor solution, the ions repelled each other which inhibit their ability to cap or interact with ZnO growing species [27]. The citrate anions can adsorb the positive charged Zn, thus suppressing the crystal growth of ZnO [28]. Once the ZnO nanoparticle is synthesised and capped with citrate, they become negatively charged and resulting electrostatic repulsion where ZnO nanostructure could be repelled from the wall and transfer back to the bulk solution. But, as ZnO nanostructure reach stabilisation throughout times, no electrostatic attraction exists which result in no fouling between the nanostructure [29, 30]. The nucleation of the nanostructure could be enhanced during the citrate reduction which assembles the ZnO in form of the multi-molecular complex [29].

CONCLUSION

In conclusion, the reported study presented that ZnO nanostructure can be produced through the simple hydrothermal method and addition of Trisodium Citrate (TC) would enhance in producing the smaller size of ZnO nanostructures with mean diameter 8nm. Higher reaction temperature results into narrower size distribution which able to indicate that it generally has a smaller size of ZnO nanostructure. These results are due to the faster rate of ionisation that occur upon a higher reaction temperature.

ACKNOWLEDGEMENT

This work was fully financially supported by the Internal Grants RDU1703152, RDU190360 and PGRS200312 of Universiti Malaysia Pahang, Malaysia

REFERENCES

[1] T. G. Smijs and S. Pavel, "Titanium dioxide and zinc oxide nanoparticles in sunscreens: focus on their safety and effectiveness," *Nanotechnology, science and applications,* vol. 4, pp. 95-112, 2011.

[2] J. A. Ruszkiewicz, A. Pinkas, B. Ferrer, T. V. Peres, A. Tsatsakis, and M. Aschner, "Neurotoxic effect of active ingredients in sunscreen products, a contemporary review," *Toxicology Reports,* vol. 4, pp. 245-259, 2017/01/01/ 2017.

[3] P. Chaudhary, P. Singh, and V. Kumar, "Synthesis and characterization of pure ZnO and La-doped ZnO (Zn0.98La0.02O) films via novel sol-gel screen- printing method," *Optik,* vol. 158, pp. 376-381, 2018/04/01/ 2018.

[4] J.-Q. Wen, J.-M. Zhang, and Z.-Q. Li, "Structural and electronic properties of Y doped ZnO with different Y concentration," *Optik,* vol. 156, pp. 297-302, 2018/03/01/ 2018.

[5] F.-X. Xiao, S.-F. Hung, H. B. Tao, J. Miao, H. B. Yang, and B. Liu, "Spatially branched hierarchical ZnO nanorod-TiO2 nanotube array heterostructures for versatile photocatalytic and photoelectrocatalytic applications: towards intimate integration of 1D–1D hybrid nanostructures," *Nanoscale,* vol. 6, pp. 14950-14961, 2014.

[6] P. J. P. Espitia, N. d. F. F. Soares, J. S. d. R. Coimbra, N. J. de Andrade, R. S. Cruz, and E. A. A. Medeiros, "Zinc Oxide Nanoparticles: Synthesis, Antimicrobial Activity and Food Packaging Applications," *Food and Bioprocess Technology,* vol. 5, pp. 1447-1464, 2012.

[7] L. He, Y. Liu, A. Mustapha, and M. Lin, "Antifungal activity of zinc oxide nanoparticles against Botrytis cinerea and Penicillium expansum," *Microbiol Res,* vol. 166, pp. 207-15, Mar 20 2011.

[8] N. Jones, B. Ray, K. T. Ranjit, and A. C. Manna, "Antibacterial activity of ZnO nanoparticle suspensions on a broad spectrum of microorganisms," *FEMS Microbiol Lett,* vol. 279, pp. 71-6, Feb 2008.

[9] A. Sirelkhatim, S. Mahmud, A. Seeni, N. H. M. Kaus, L. C. Ann, S. K. M. Bakhori, *et al.*, "Review on Zinc Oxide Nanoparticles: Antibacterial Activity and Toxicity Mechanism," *Nanomicro Lett,* vol. 7, pp. 219-242, 2015.

[10] Z. L. Wang, "ZnO Nanostructure " 2004.

[11] J.-C. Chen and C.-T. Tang, "Preparation and application of granular ZnO/Al2O3 catalyst for the removal of hazardous trichloroethylene," *Journal of Hazardous Materials,* vol. 142, pp. 88-96, 2007/04/02/ 2007.

[12] P. Basnet, T. Inakhunbi Chanu, D. Samanta, and S. Chatterjee, "A review on bio-synthesized zinc oxide nanoparticles using plant extracts as reductants and stabilizing agents," *Journal of Photochemistry and Photobiology B: Biology,* vol. 183, pp. 201-221, 2018/06/01/ 2018.

[13] M. Joulaei, K. Hedayati, and D. Ghanbari, "Investigation of magnetic, mechanical and flame retardant properties of polymeric nanocomposites: Green synthesis of MgFe2O4 by lime and orange extracts," *Composites Part B: Engineering,* vol. 176, p. 107345, 2019/11/01/ 2019.

[14] P. Mahajan, A. Sharma, B. Kaur, N. Goyal, and S. Gautam, "Green synthesized (Ocimum sanctum and Allium sativum) Ag-doped cobalt ferrite nanoparticles for antibacterial application," *Vacuum*, vol. 161, pp. 389-397, 2019/03/01/ 2019.

[15] K. C. Suresh, S. Surendhiran, P. Manoj Kumar, E. Ranjth Kumar, Y. A. S. Khadar, and A. Balamurugan, "Green synthesis of SnO2 nanoparticles using Delonix elata leaf extract: Evaluation of its structural, optical, morphological and photocatalytic properties," *SN Applied Sciences*, vol. 2, p. 1735, 2020/09/25 2020.

[16] A. E. D. Mahmoud, "Nanomaterials: Green Synthesis for Water Applications," in *Handbook of Nanomaterials and Nanocomposites for Energy and Environmental Applications*, O. V. Kharissova, L. M. T. Martínez, and B. I. Kharisov, Eds., ed Cham: Springer International Publishing, 2020, pp. 1-21.

[17] T. Ahmad, "Reviewing the Tannic Acid Mediated Synthesis of Metal Nanoparticles," *Journal of Nanotechnology*, vol. 2014, pp. 1-11, 2014.

[18] A. Krol, P. Pomastowski, K. Rafinska, V. Railean-Plugaru, and B. Buszewski, "Zinc oxide nanoparticles: Synthesis, antiseptic activity and toxicity mechanism," *Adv Colloid Interface Sci*, vol. 249, pp. 37-52, Nov 2017.

[19] N. Padmavathy and R. Vijayaraghavan, "Enhanced bioactivity of ZnO nanoparticles-an antimicrobial study," *Sci Technol Adv Mater*, vol. 9, p. 035004, Jul 2008.

[20] R. Wahab, S. G. Ansari, Y. S. Kim, H. K. Seo, G. S. Kim, G. Khang, *et al.*, "Low temperature solution synthesis and characterization of ZnO nano-flowers," *Materials Research Bulletin*, vol. 42, pp. 1640-1648, 2007.

[21] L. Ge, X. Jing, J. Wang, J. Wang, S. Jamil, Q. Liu, *et al.*, "Trisodium citrate assisted synthesis of ZnO hollow spheres via a facile precipitation route and their application as gas sensor," *Journal of Materials Chemistry*, vol. 21, pp. 10750-10754, 2011.

[22] Y. Bao, C. Wang, and J. Ma, "Trisodium citrate as bridging and suppressing agent to control synthesis of ZnO hollow hierarchical microspheres and their photocatalytic properties," *Ceramics International*, vol. 42, pp. 1746-1755, 2016/01/01/ 2016.

[23] S. Baruah and J. Dutta, "Hydrothermal growth of ZnO nanostructures," *Science and Technology of Advanced Materials*, vol. 10, p. 013001, 2009/01/01 2009.

[24] Y.-k. Qin, X.-p. Guo, F.-y. Tou, H. Pan, J.-n. Feng, J. Xu, *et al.*, "Cytotoxicity of TiO2 nanoparticles toward Escherichia coli in an aquatic environment: effects of nanoparticle structural oxygen deficiency and aqueous salinity," *Environmental Science: Nano*, vol. 4, pp. 1178-1188, 2017.

[25] Y.-y. She, J. Yang, and K.-q. Qiu, "Synthesis of ZnS nanoparticles by solid-liquid chemical reaction with ZnO and Na2S under ultrasonic," *Transactions of Nonferrous Metals Society of China*, vol. 20, pp. s211-s215, 2010/05/01/ 2010.

[26] A. K. Thottoli and A. K. A. Unni, "Effect of trisodium citrate concentration on the particle growth of ZnS nanoparticles," *Journal of Nanostructure in Chemistry*, vol. 3, p. 56, 2013/07/15 2013.

[27] S. Suwanboon, P. Amornpitoksuk, and C. Randorn, "Effect of tartaric acid as a structure-directing agent on different ZnO morphologies and their physical and photocatalytic properties," *Ceramics International*, vol. 45, pp. 2111-2116, 2019/02/01/ 2019.

[28] Y. Bao, C. Wang, and J.-z. Ma, "Morphology control of ZnO microstructures by varying hexamethylenetetramine and trisodium citrate concentration and their photocatalytic activity," *Materials & Design*, vol. 101, pp. 7-15, 2016/07/05/ 2016.

[29] H. Huang, H. d. Toit, M. O. Besenhard, S. Ben-Jaber, P. Dobson, I. Parkin, *et al.*, "Continuous flow synthesis of ultrasmall gold nanoparticles in a microreactor using trisodium citrate and their SERS performance," *Chemical Engineering Science*, vol. 189, pp. 422-430, 2018/11/02/ 2018.

[30] J.-W. Park and J. S. Shumaker-Parry, "Structural Study of Citrate Layers on Gold Nanoparticles: Role of Intermolecular Interactions in Stabilizing Nanoparticles," *Journal of the American Chemical Society*, vol. 136, pp. 1907-1921, 2014/02/05 2014.