



Role of Stabilizing Agents on Modifying Size and Morphology of ZnO Nanoparticles Synthesized *via* Sol-Gel Route

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In the present study, the synthesis of ZnO nanoparticles through sol-gel route by using different stabilizing agents namely polyethylene glycol, polyvinyl alcohol and starch have been reported. The particle size calculated from the diffraction pattern of nano ZnO and Al doped ZnO synthesized using starch as stabilizing agent is found to be 19 and 13 nm, respectively. While compared with the other stabilizing agent like poly(vinyl alcohol) and poly(ethylene glycol) that the growth of ZnO nanoparticles size has controlled in starch. In case of poly(vinyl alcohol) and starch stabilized nano ZnO shows the formation of spherical ellipse ZnO nanoparticles without any agglomeration. Size and morphological studies were performed using X-ray diffraction, Fourier transform infrared spectroscopy (FTIR), scanning electron microscope (SEM) with energy dispersive X-ray (EDX) analysis and high resolution transmission electron microscope (TEM). The synthesized ZnO possess highly crystalline wurtzite structure. The morphological study clearly reveals that the nano ZnO particle shows spherical elliptical shape.

Keywords: Nano ZnO, Stabilizing agent, Sol-gel route, XRD.

INTRODUCTION

Recently, there has been a growing stipulate for the growth of nano sized semiconductors than bulk due to their noteworthy electrical and optical properties. Zinc oxide has attracted much interest as a potential nanomaterial due to the inexpensive and n-type semi conductor of wurtzite structure with wide band gap of 3.2-3.3 eV. ZnO have widely been used in various applications such as solar cells, photo catalyst, biosensors, photo luminescent material and antimicrobial activity [1-5]. Several methods were adopted for the production of nanoscale ZnO such as vapour deposition [6], precipitation [7], sonochemical method [8], laser ablation [9], oxidation process [10], solvothermal and hydrothermal methods [11], a polymerization method [12] and sol-gel synthesis [13].

Among these methods, sol-gel technique is inexpensive, simple and produces high purity with large surface area of ZnO nanoparticles. In regulate to prove ZnO nanoparticles from endure impulsive development and aggregation, many scientist have attempted to utilize a variety of organic ligands [14]. Adding organic compounds such as poly(ethylene glycol)

(PEG) [15,16], poly(vinyl alcohol) (PVA) cetyltrimethyl ammonium bromide (CTAB) [17], starch [18] are some of the protecting as well as stabilizing agents make use of to organize the growth, shape and dimension of the nanoparticles. Hence, present work designed to develop a simple route to prepare ZnO nanoparticles utilizing various stabilizing agents such PEG, PVA and starch by sol-gel method. Among the stabilizing agent, starch has a superior chemical reactivity compared to other polymerization agents and it provide as a terminator mounting ZnO nanoparticles owing to its long chain made with glucose, consequently, the atom cannot approach jointly easily and nanosized ZnO particles are acquired. The crystalline nature, morphology and size were investigated by using X-ray diffraction (XRD), Fourier transform infrared (FT-IR) spectroscopy, scanning electron microscope (SEM) and transmission electron microscope (TEM), respectively.

EXPERIMENTAL

Zinc acetate dihydrate (Sigma-Aldrich), Starch (Sigma-Aldrich), ammonium hydroxide (Sigma-Aldrich), ethanol

(Sigma-Aldrich), poly(ethylene glycol), poly(vinyl alcohol) and aluminium chloride monohydrate (Sigma-Aldrich) were used. Distilled water was used throughout this study.

Synthesis of ZnO by sol-gel method: To prepare pure ZnO NPs, about 2.112 g of zinc acetate dihydrate dissolved in 100 mL of distilled water and heated for few seconds to get a clear solution. Then it refluxed at 78 °C for 1 h. Meanwhile, 5 g of PEG liquefy in 100 mL of demineralized water and mixed for 0.5 h 75 °C to attain homogenous gelly solution. Then the refluxed reaction mixture (sol) was cooled to room temperature. The pH of the acquired sol is maintained to 7.2 by using 15 to 20 drops of ammonium hydroxide. Then this sol was added to the PEG solution by continuing vigorous mixing under magnetic stirrer. After the mixture achieved gelatinized state, it kept aging for few hours at room temperature. Then the sol-gel mixture filtered through the filter paper of Whatmann No. 42 and the gelatinous mixture dried by hot air oven at 90-100 °C for 2-4 h. Dried mixture is calcined in muffle furnace. At the end, the materials were attained with ease by calcining ZnO-PEG at 700 °C for 5 h. The same procedure was repeated for PVA and starch stabilizers.

Synthesis of Al doped ZnO NPs by sol-gel method: The Al impregnated ZnO nanoparticles were synthesized by the sol-gel method using aluminium trichloride as metal precursor and ethanol as a solvent. 10.39 g of zinc acetate dihydrate and 0.006 g of AlCl_3 in 100 mL ethanol was refluxed at 70 °C. Subsequently 2 g of starch is dissolved in 100 mL hot distilled water at 60 °C. Then starch solution is added to the obtained solution drop-by-drop stirred constantly using the magnetic stirrer for 1 h until the dissolution occurs. Then NH_4OH is added to maintain the pH of the sol around 7.2. After the completion of the reaction the solution was allowed to settle down for 24 h. The supernatant solution was discarded and the remaining solution was filtered by Whatman filter paper 40 and centrifuged. The powdered Al doped ZnO nanoparticles were achieved at 90 °C. Then dried powder is calcinated above 700 °C for 6 h in muffle furnace.

Characterization techniques: The crystalline nature of ZnO-starch nanoparticles was analyzed by using XRD technique. The diffraction intensity was identified between 10° to 90° (2 θ). The absorption peaks of ZnO-starch nanoparticles were studied using FTIR spectrophotometer and recorded over the wave number of 4000-400 cm^{-1} . The surface morphology, structure and size of ZnO-starch nanoparticles were studied by utilizing scanning electron microscope (SEM) and transmission electron microscope (TEM), respectively.

RESULTS AND DISCUSSION

XRD: The XRD patterns of ZnO-starch nanoparticles and Al doped ZnO-starch nanoparticles were shown in Fig. 1. The strong sharp diffraction peaks indicate that the ZnO nanoparticles are well crystallized. The well resolved diffraction peaks at 31.84°, 34.56°, 36.42°, 47.51°, 56.72°, 62.65°, 66.43°, 68.23°, 69.45°, 72.75°, 76.80° and 89.83° which corresponds to ZnO-starch nanoparticles. Similarly, the diffraction patterns of the Al doped ZnO-starch nanoparticles, which shows the peaks at 15.81°, 22.10°, 27.82°, 29.4°, 31.6°, 34.3°, 36.1°, 47.4°, 56.5°, 62.8°, 66.3°, 67.9°, 69.0°, 76.9° and 89.7°,

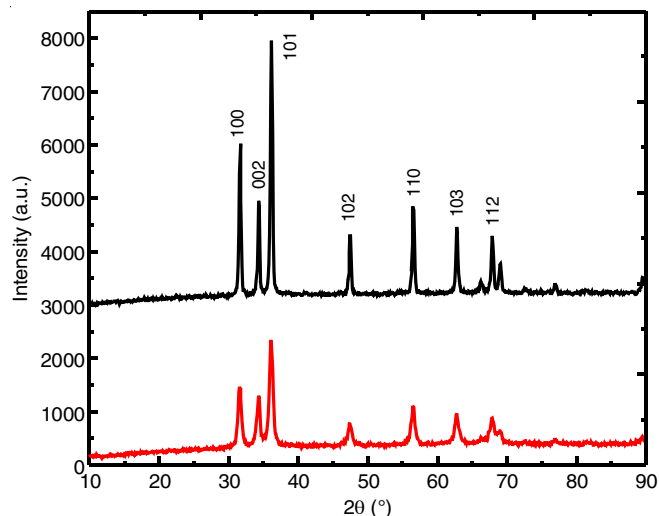


Fig. 1. XRD patterns of ZnO-starch nanoparticles and Al doped ZnO-starch nanoparticles

respectively. From this XRD pattern, we observed that the peaks assigned to diffractions from various planes correspond to the hexagonal wurtzite structure of ZnO [18]. The average particle size (D) were determined utilizing Scherrer's equation

$$D = 0.9\lambda / (\beta \cos \theta) \quad (1)$$

where λ , β and θ are the X-ray wavelength (0.154 nm), full width at half maxima (FWHM) of the diffraction peak and the Bragg's diffraction angle, respectively. By applying the above formula the crystalline ZnO nano particles synthesized through stabilizers of PEG, PVA and Starch were found to be 25 ± 7 , 23 ± 7 and 19 ± 5 nm, respectively and also the size of the Al doped ZnO nanoparticles decreased in the particles size 13 nm. This may be owed to reduced sintering rate that happen through the sol-gel method [19]. These results confirm that the growth of ZnO nanoparticles size and Al loaded ZnO nanoparticles, which can be controlled in Starch than PVA and PEG. Starch act as a good stabilizing agents when compared with PVA and PEG.

FT-IR: FT-IR spectrum of ZnO NPs obtained by sol-gel method using starch as stabilizing agent, which is shown in Fig. 2. The characteristic peaks between 3788 and 3350 cm^{-1} of all the three samples are corresponding to the O-H stretching vibration of $\text{Zn}(\text{OH})_2$. It can be contributed to the free -OH as well as the O-H bonded stretching. The peaks at 1483-1397 cm^{-1} and 720 cm^{-1} are related to the C-H bending vibrations of CH_2 , CH_3 groups in various stabilizing agents. The stretching symmetric mode C=O of vibration bands due to zinc acetate dihydrate of PEG, PVA and starch are obtained at 1570, 1570 and 1569 cm^{-1} , respectively. The peaks from the range of 1123 to 986 cm^{-1} corresponds to broad C-O stretching vibration. The peak at 720 and 719 cm^{-1} also at 657 to 656 cm^{-1} arises due to the out of plane bending of O-H bond. The band of Starch shows exact peak of ZnO and Al doped ZnO at 435 cm^{-1} and 389.90 cm^{-1} , respectively is attributed to the stretching of ZnO and also due to the presence of Al into ZnO lattice [20].

SEM with EDX: The surface morphology and chemical composition of ZnO-starch nanoparticles and Al doped ZnO-starch nanoparticles were investigated using scanning electron microscopy with an energy dispersive X-ray (EDX) spectro-

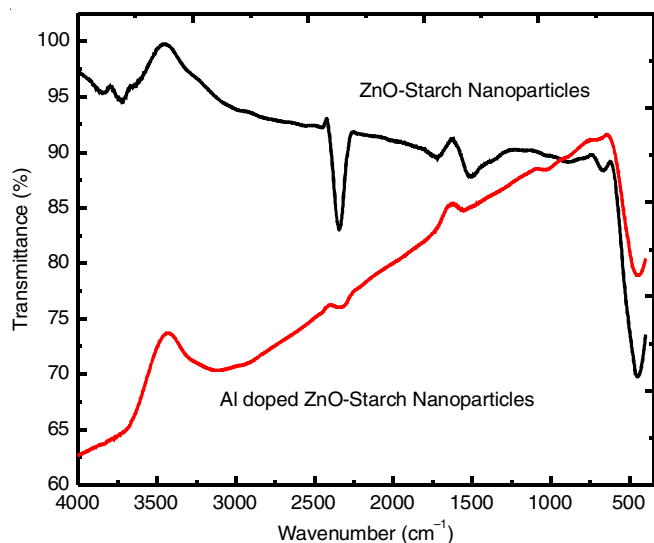


Fig. 2. FT-IR spectra of ZnO-starch nanoparticles and Al doped ZnO-starch nanoparticles

scopy analysis (Fig. 3). It was clearly observed that the most of particles are well defined hexagonal structure of ZnO-starch nanoparticles and Al doped ZnO-starch nanoparticles (Fig. 3a & 3b). To determine the purity and chemical composition of

the sample, energy dispersive X-ray (EDX) analysis was carried out and shown in Fig. 3c. The results indicate that Al doped ZnO-starch nanoparticles obtained of high purity. The external of the Al doped ZnO-starch nanoparticles also confirmed elements of C, O, Zn and Al. The EDX spectra shows that the sample consists of exclusively Zn = 72.94 %, Al = 1.31 % and O = 25.75 %. So, considering the detection of elements in the sample, we obtained high purity of Al doped ZnO nanomaterial. The starch stabilized nano ZnO shows uniform size distribution and high crystalline nature with reduced particle size [21]. These results are consistent with the XRD data.

TEM: The structure and size of ZnO-starch and Al loaded ZnO-starch nanoparticles was clearly seen in the TEM images and presented in Fig. 4. Fig. 4a illustrates ZnO-starch nanoparticles were dissolved in the solution system at the nanoscale with uniform and the particles size ranges approximately 19-25 nm. The formed ZnO nanoparticles might be bind with hydroxyl (O-H) groups on the starch molecules to form uniform size of ZnO-starch nanoparticles without aggregation [22]. The TEM image of Al doped ZnO-starch nanoparticles were shown in Fig. 4b, which clearly revealed that the aluminium particles are well dispersed and appear to be black dots in the image and also show the particles size 13 nm.

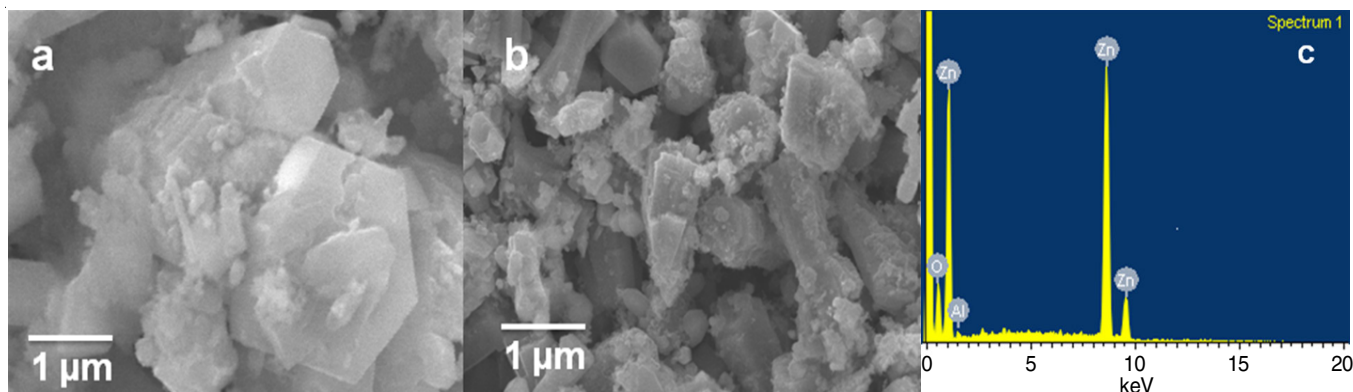


Fig. 3. SEM image of (a) ZnO-starch nanoparticles, (b) Al doped ZnO-starch nanoparticles and (c) EDX analysis of Al doped ZnO-starch nanoparticles

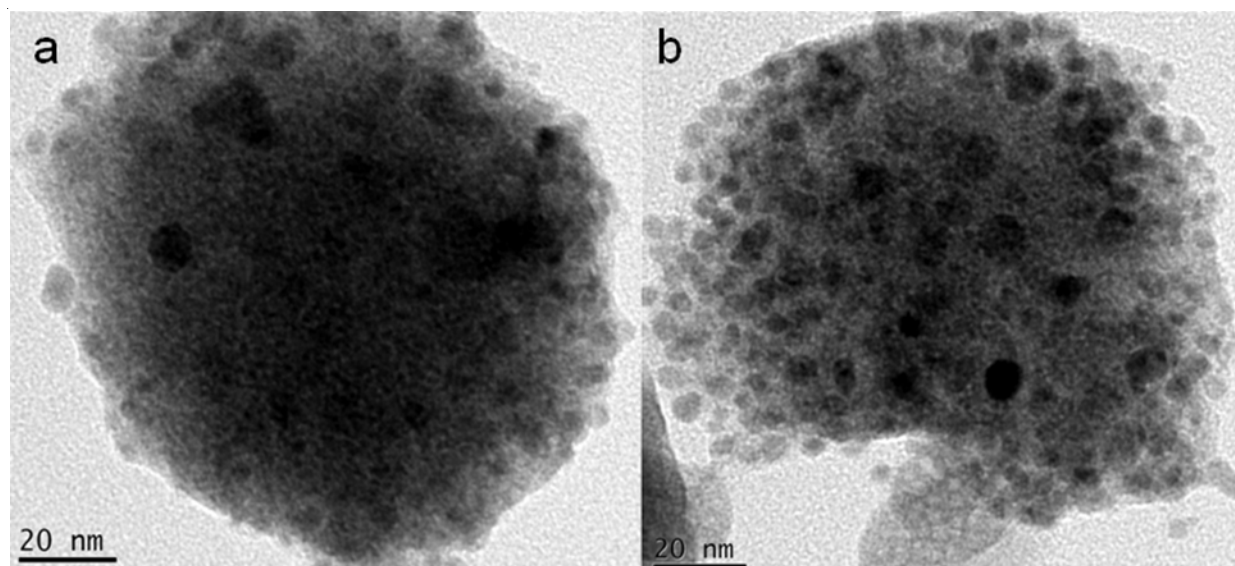


Fig. 4. TEM images of ZnO-starch nanoparticles and Al doped ZnO-starch nanoparticles

Conclusion

In summary, size and shape controlled ZnO nanoparticles and Al loaded ZnO NPs were successfully synthesized using different stabilizing agents like PEG, PVA and starch. Based on the synthesis carried out and from the characterization results obtained were ZnO-starch and Al doped ZnO nanoparticles were successfully produced through single step sol-gel method using PEG, PVA and starch as stabilizer and their yield is high. The FT-IR and XRD results clearly show the formation of ZnO NPs and Al doped ZnO NPs are highly pure. The average crystalline size is reduced by starch around 19 nm of ZnO where as Al doped ZnO still reduced in the size 13 nm. The obtained ZnO nano particles seem to be spherical ellipse shape. Hence the synthesized nano ZnO and Al doped ZnO could be used in optoelectronic devices, solar cells as photo catalysts and in membrane applications.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

REFERENCES

1. J.H. Jang, J.H. Park and S.G. Oh, *J. Ceram. Process. Res.*, **10**, 783 (2009).
2. S. Rani, P. Suri, P. Shishodia and R. Mehra, *Sol. Energy Mater. Sol. Cells*, **92**, 1639 (2008); <https://doi.org/10.1016/j.solmat.2008.07.015>.
3. J.-H. Yum, S.-S. Kim, D.-Y. Kim and Y.-E. Sung, *J. Photochem. Photobiol. Chem.*, **173**, 1 (2005); <https://doi.org/10.1016/j.jphotochem.2004.12.023>.
4. X.-F. Wang, O. Kitao, E. Hosono, H. Zhou, S. Sasaki and H. Tamiaki, *J. Photochem. Photobiol. Chem.*, **210**, 145 (2010); <https://doi.org/10.1016/j.jphotochem.2010.01.004>.
5. L. Dong, M.M. Craig, D. Khang and C. Chen, *J. Nanotechnol.*, **Article ID 816184** (2012); <https://doi.org/10.1155/2012/816184>.
6. R. Yousefi, M.R. Muhamad and A.K. Zak, *Curr. Appl. Phys.*, **11**, 767 (2011); <https://doi.org/10.1016/j.cap.2010.11.061>.
7. C.L. Kuo, C.L. Wang, H.H. Ko, W.S. Hwang, K.M. Chang, W.L. Li, H.H. Huang, Y.H. Chang and M.C. Wang, *Ceram. Int.*, **36**, 693 (2010); <https://doi.org/10.1016/j.ceramint.2009.10.011>.
8. C. Deng, H. Hu, G. Shao and C. Han, *Mater. Lett.*, **64**, 852 (2010); <https://doi.org/10.1016/j.matlet.2010.01.039>.
9. R. Zamiri, A. Zakaria, H.A. Ahangar, M. Darroudi, A.K. Zak and G.P.C. Drummen, *J. Alloys Compd.*, **516**, 41 (2012); <https://doi.org/10.1016/j.jallcom.2011.11.118>.
10. Z.H. Wang, D.Y. Geng, Z. Han and Z.D. Zhang, *Mater. Lett.*, **63**, 2533 (2009); <https://doi.org/10.1016/j.matlet.2009.08.044>.
11. R. Razali, A.K. Zak, W.H.A. Majid and M. Darroudi, *Ceram. Int.*, **37**, 3657 (2011); <https://doi.org/10.1016/j.ceramint.2011.06.026>.
12. P. Jajarmi, *Mater. Lett.*, **63**, 2646 (2009); <https://doi.org/10.1016/j.matlet.2009.08.062>.
13. A.K. Zak, M.E. Abrishami, W.H.A. Majid, R. Yousefi and S.M. Hosseini, *Ceram. Int.*, **37**, 393 (2011); <https://doi.org/10.1016/j.ceramint.2010.08.017>.
14. A. Khorsand Zak, W.H. Abd. Majid, M.R. Mahmoudian, M. Darroudi and R. Yousefi, *Adv. Powder Technol.*, **24**, 618 (2013); <https://doi.org/10.1016/j.apt.2012.11.008>.
15. B. Cheng and E.T. Samulski, *Chem. Commun.*, **8**, 986 (2004); <https://doi.org/10.1039/b316435g>.
16. Y. He, J. Wang, W. Sang, R. Wu, L. Yan and Y. Fang, *Acta Chim. Sin.*, **63**, 1037 (2005).
17. H.J. Zhai, W.H. Wu, F. Lu, H.S. Wang and C. Wang, *Mater. Chem. Phys.*, **112**, 1024 (2008); <https://doi.org/10.1016/j.matchemphys.2008.07.020>.
18. J. Ma, W. Zhu, Y. Tian and Z. Wang, *Nanoscale Res. Lett.*, **11**, 200 (2016); <https://doi.org/10.1186/s11671-016-1404-y>.
19. M. Mazaheri, A.M. Zahedi and S.K. Sadrmehzad, *J. Am. Ceram. Soc.*, **91**, 56 (2008); <https://doi.org/10.1111/j.1551-2916.2007.02029.x>.
20. A. Vanaja, G.V. Ramaraju and S. Rao, *Indian J. Sci. Technol.*, **9**, 1 (2016); <https://doi.org/10.17485/ijst/2016/v9i12/87013>.
21. J.L. Konne and K. Okpara, *Energy Environ. Res.*, **4**, 25 (2014); <https://doi.org/10.5539/eer.v4n1p25>.
22. H. Usui, Y. Shimizu, T. Sasaki and N. Koshizaki, *J. Phys. Chem. B*, **109**, 120 (2005); <https://doi.org/10.1021/jp046747j>.