



Studies on Scale-up of Synthesis of ZnO Nanoparticles

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Synthesis of spherical ZnO nanoparticles by room temperature chemical precipitation method was scaled up from a batch volume of 200 mL to batch volume of 500 mL, 1 L, 2 L and 5 L. Electron microscopy results reveal spherical morphology of the particles with sizes in the range of 20-40 nm at all batch volumes (scales). X-ray diffraction studies showed that the ZnO nanopowders synthesized at all batch volumes had hexagonal Wurtzite structure with a similar crystallite size. The yield of ZnO nanoparticles increased linearly with batch volume. The scale up results in increased yield at lower time consumption.

Keywords: ZnO, Scale up, Nanoparticles, Synthesis, Precipitation.

INTRODUCTION

With development in the new strategies for nanomaterials synthesis, characterization techniques and owing to their impressive physical, chemical and catalytic properties, nanomaterials have gained significant importance in the past two decades. Materials with dimensions in the range of 1-100 nm (nanomaterials) are significantly different from bulk materials¹. As materials reach nanoscale dimensions, they turn to those with attracting properties such as finite size effects and surface or interface effects. Size-dependent properties of the nanoparticles are very striking and are different from that of bulk materials.

Nanomaterials include nanocrystals and clusters, nanowires, nanotubes, nanoporous solids, 2-Dimensional arrays and 3-dimensional structures. Nanomaterials might be metals, semiconductors, magnetic materials, ceramic oxides, carbon, zeolites, chalcogenides, *etc.*¹.

Among the various types of nanomaterials, transition metal oxides are widely used for preparation of nanofluids²⁻⁵ and sensing layers⁶⁻⁸. Zinc oxide stands as a good exemplar. Zinc oxide is a wide band gap semiconductor. The crystalline Wurtzite structure of the ZnO nanoparticles renders it to be used in various applications. Zinc oxide nanoparticles offers various benefits due to its extensive range of properties and are presently used in food additives, rubber manufacture⁹, biosensors, solar cell¹⁰, gas sensors¹¹, textiles¹², photodiodes, photocatalysis¹³, solar cells¹⁴, cement manufacture¹⁵, food packaging¹⁶, coatings¹⁷ and antimicrobials¹⁸.

Synthesis of ZnO nanoparticles as well as other nanoparticles are interesting research area of researchers. Zinc oxide nanoparticles have been synthesized by various methods like chemical precipitation method¹⁹⁻²¹, hydrothermal and solvothermal methods^{14,22}, in structured medium, vapour phase reactions^{23,24}, synthesis in structured medium²⁵. Vapour deposition method has been developed to synthesize complex structured nanoparticles like flower-like and web-like agglomerates which require multiple steps, sophisticated equipment and high temperature for obtaining the final nanostructure.

Due to high requirement of ZnO nanoparticles in the applied nanotechnology, there is need for synthesis procedures giving high yields. However, most of the synthesis procedures are often time consuming and results in lesser yields. Hence, it is essential to scale up the synthesis procedure, which should also be cost effective. Large-scale preparation of nanoparticles is challenging. The parameters used in primary scale have to be modulated as per the requirements for large scale without compromising the quality of nanoparticles. However, in higher scales, it is difficult to maintain the changes²⁶. Spray route, gas condensation method²⁷, esterification²⁸ are usually adopted methods for synthesis scale up.

For scaling up a synthesis procedure, a process with maximum control should be selected in order to avoid scale up loss. Criteria for selection of a procedure for scale up includes less time consumption, higher yield and relatively easier control. Besides involving simple steps, chemical precipitation method also gives high yield and stands as the best method in a commercial perspective.

In this report, ZnO nanoparticles were synthesized at relatively large scale using room temperature chemical precipitation method. Zinc nitrate hexahydrate and ammonium carbonate were used for synthesis of ZnO nanoparticles and the precipitation reaction was thermodynamically favorable at room temperature. Hence, there is no need for control of temperature and the challenge in controlling the reaction temperature is avoided. Moreover, precipitation method yields large volume of nanoparticles compared to other synthesis methods. Separation of nanoparticles from the reaction medium is also relatively easier. The synthesis method has its own advantages, such as low-processing cost, high quality, isothermal & ambient temperature reaction, less time consumption and high yield, hence making it selective for the up scaling of a synthesis. In the present study, step-wise scale up of synthesis of ZnO has been performed with the yield at the highest scale, about 25 times greater than that obtained at the lowest scale.

EXPERIMENTAL

Zinc nitrate hexahydrate, ammonium carbonate and methanol were purchased from Merck (India), Fisher Scientific (India) and Loba Chemie (India), respectively. Deionized water was used for the experiments.

Nanoparticle synthesis: Synthesis procedure elaborated elsewhere^{19,29-31} was adopted for scaling up. Zinc oxide nanoparticles were synthesized by the room temperature chemical precipitation method in which zinc nitrate hexahydrate has been used as the precursor. Equimolar solutions of ammonium carbonate and zinc nitrate hexahydrate were prepared. Zinc nitrate solution was added to ammonium carbonate in drop wise under continuous stirring. The precipitate was filtered and then washed with water for several times and then with methanol. The sample was dried at 80°C for 5 h. The dried powder was calcined^{19,29-31} at 550 °C for 2 h.

Nanoparticle synthesis scale-up: Nanoparticle synthesis scale-up was carried out from 200 mL scale to 5 L scale. ZnO nanoparticles were synthesized in various batch volumes of 200 to 500 mL, 1, 2 and 5 L in a baffled, cylindrical batch reactor. The precursor solution was added dropwise to the ammonium carbonate solution under continuous stirring. Overhead mechanical stirrers were used for obtaining the continuous mixing. Volume of precursor solution to be added to ammonium carbonate solution was calculated using stoichiometric ratio. Care was taken to ensure constant flow rate of precursor solution and thorough mixing of reactants. The precipitate was further processed as explained above to obtain ZnO nanoparticles.

Electron microscopy: Morphological characterization of synthesized powder obtained from each scaling was performed using the cold Field Emission Scanning Electron Microscope (JSM 6701F, JOEL, Japan). The accelerating voltage was 3 kV. The powder samples were sputter coated with gold and mounted on a brass stub, which was then loaded into the sample chamber and imaged.

X-ray diffraction: It is essential to study the crystalline nature of ZnO nanoparticles owing to the importance of crystallinity of nanoparticles in various applications. X-ray diffrac-

tometer (D8 Focus, Bruker, Germany) was used to analyze the crystalline nature of the particles obtained from different scale up volumes with CuK α X-ray. Analysis was performed over a 2 theta range of 10-60° with a step size of 0.01°. Morphological and crystalline natures of the nanoparticles obtained from different scale up volumes were characterized to study the influence of scale (reaction volume) on particle morphology.

RESULTS AND DISCUSSION

Nanoparticle synthesis scale-up: The main aim of this work was to scale up the batch volume for synthesis from 200 mL to 5 L. Synthesis was also carried out at intermediate batch volumes 500 mL, 1 and 2 L to ascertain the correlation between batch volumes.

Time consumed for precursor addition for different batch volumes was compared with that required for 200 mL batches (Fig. 1). About 4 h was required for precursor addition in 200 mL batch volume. The scaling up was done to 25 times. It can be estimated that time required for precursor addition to synthesize ZnO nanoparticles in reaction volume of 5 L would be about 100 h, considering that the precursor addition time for 200 mL batch was 4 h. However, in the scaling up procedure, time taken for 5 L batch was 11 h only. For the intermediate scales of reaction volumes (500 mL to 2 L), similar reduction in precursor addition time was observed.

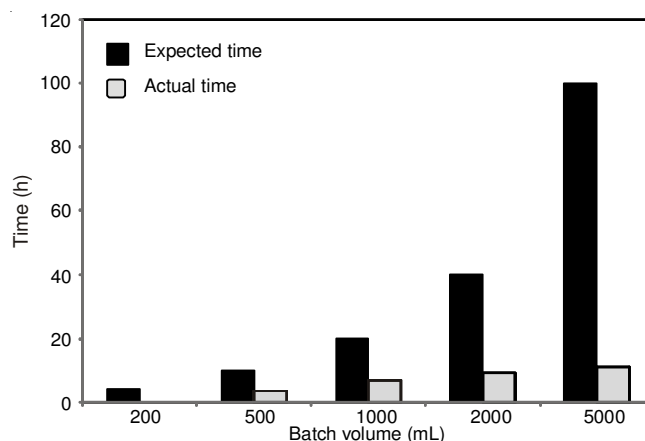


Fig. 1. Time requirement for synthesis scale-up and comparison between expected time and actual time for each scale

Fig. 2 shows that yield of ZnO nanoparticles linearly increased from 200 mL batch to 5 L batch. Linear increase in yield with batch volume indicates that there is no scale up loss and the synthesis procedure has been effectively scaled up. Yield from 200 mL batch was 1.304 g. and that of from 5L batch was 35.586 g. Thus from a single batch, 30-35 g of ZnO nanoparticles can be synthesized with precursor addition time of 11 h.

Morphology: Scanning electron micrographs of synthesized nanoparticles shown in Fig. 3 reveal that the particles were of well defined spherical morphology and were present in the form of aggregates.

The uniform spherical morphology of the nanoparticles is preferable for various applications. Morphology of the nanoparticles was found to be uniform irrespective of scale

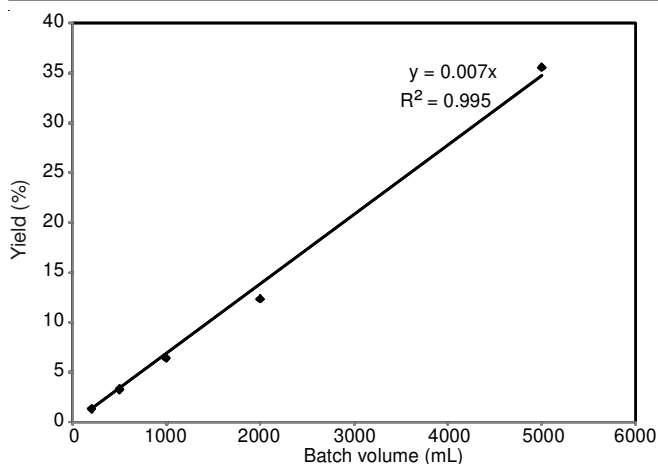


Fig. 2. Yield obtained per scaling of the synthesis scale-up

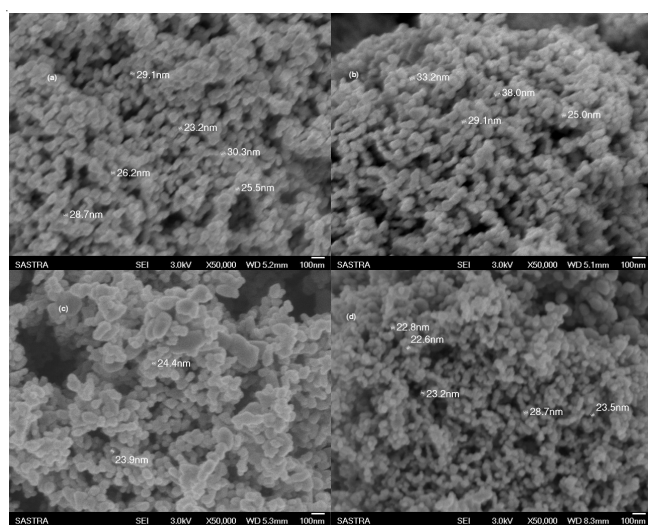


Fig. 3. (a-d) Scanning electron micrographs of ZnO nanoparticles synthesized at scale-up volumes of 200 mL, 500 mL, 2 L, 5 L at magnification of 50,000

up batch volumes. Particles of size range 20–40 nm can be seen in scanning electron micrographs of all scale up volumes. By using room temperature chemical precipitation method, it was possible to maintain the nanostructure of the particle even at larger scales. However, at larger scales (2 L, 5 L), a small fraction of larger size particles can be seen which might be due to the improper mixing of the reactants in certain areas of the reactor vessel. This shows that reactants should be mixed still more effectively in order to avoid the formation of larger size particles.

X-ray diffractometry: X-ray diffraction spectra of ZnO nanoparticles synthesized at different batch volumes are shown in Fig. 4. XRD spectra shows that ZnO nanoparticles synthesized at various batch volumes were highly crystalline. XRD spectra of nanopowders of all batch volumes match with the PCPDFWIN no. 89-1397 and are of hexagonal Wurtzite phase. Crystallite sizes of the nanoparticles were calculated using Scherrer formula and were found to be similar for all batch volumes and in well accordance with scanning electron micrographs. Average crystallite size of ZnO nanoparticles synthesized at different batch volumes was 36.19 ± 3 nm. This shows that scaling up of synthesis procedure has not influenced the

crystallinity of the nanoparticles. When nanoparticles are dispersed in liquids, the interactions between nanoparticles themselves and between nanoparticles and liquid are influenced by particle surface. It is widely known that even at the scale of micrometer or millimeter sized particles, the interactions between solid particles and fluid are influenced by particle size³²⁻³⁸. The size control achieved at all the scales of syntheses demonstrates the success of scale up attempted in this work.

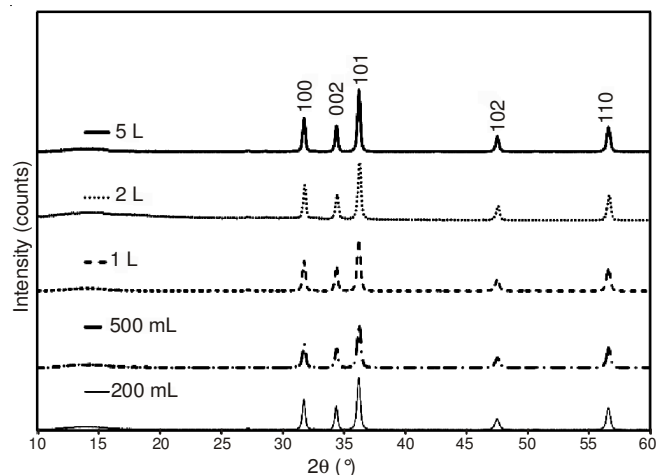


Fig. 4. X-ray diffraction pattern of ZnO nanoparticles synthesized at different batch volumes

Conclusion

Room temperature chemical precipitation method for ZnO nanoparticle synthesis has been scaled up without any yield or time loss. Spherical morphology and particle size range of 20–40 nm was achieved at all scale up batch volumes by ensuring uniform mixing and controlled addition of precursor solution. Crystalline Wurtzite structure was obtained for ZnO nanoparticles synthesized starting from lower scale up volume to higher scale up volume. Scaling up of ZnO synthesis has not altered the properties of nanoparticles. From a single batch volume of 5 L, 30–35.5 g ZnO nanoparticles can be prepared. This method has great potential to be further scaled up and commercialized. Presence of a small fraction of larger particles emphasizes the requirement of well stirred system at larger batch volumes.

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