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Synthesis of ZnO Nanoparticles by Co-Precipitation Method: Effect of Washing on the Purity of the Nanoparticles

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Abstract

The objective of this study was to investigate the influence of washing on purity of the synthesized ZnO nanoparticles (NPs). Here, co-precipitation method was followed to synthesize ZnO NPs, which involved washing and annealing of $Zn(OH)_2$ precipitates in facilitating the conversion into ZnO. XRD analysis indicated the formation of hexagonal wurtzite crystal structure of ZnO. However, an unwanted peak at 29.4° was observed, which prompted further deeper analysis. Rietveld analysis performed to identify the root cause revealed that the presence of nitrate salt, which was formed during the precipitation reaction between $Zn(NO_3)_2.6H_2O$ and NaO_3, was accountable for the extra peak. Inadequate washing was suspected to be the reason and subsequent thorough washing resulted in disappearance of the extra peak and the emergence of single phase ZnO NPs. These results highlight the importance of thorough washing when using the co-precipitation approach to obtain pure ZnO nanoparticles free of any undesirable contaminants. The effect of increasing annealing temperature was also found to be effective to resolve this issue with limitation of crystallite size control.

Keywords: Co-Precipitation, Washing, Annealing, Precipitates, Rietveld.

1. Introduction

Nanocrystalline materials have grown as a promising research area over the last few decades. Extensive applications in various sectors such as solar cells, varistors, gas sensors, ion-insertion batteries and room temperature ultraviolet lasers are the primary attraction for this enhanced inquisitiveness of researchers [1-3] . Among various semiconductor metal oxides, ZnO have demonstrated to be a potential candidate owing to its greater natural abundance, low cost, non-toxicity, considerable absorption efficiency and quantum confinement behaviour in an attainable size range [4]. Besides, this n-type semiconductor exhibits wide bandgap (~3.37 eV) and greater exciton binding energy (60 meV) at room temperature [4]. ZnO NPs show distinctive physicochemical characteristics and transparent conducting properties in the visible range of the solar spectra [5] which include size, shape, crystal structure and porosity [4].

Numerous synthesis routes have been reported for ZnO NPs preparation over the years including thermal transport method, sol-gel method, co-precipitation method, pulsed laser deposition, hydrothermal method, and chemical vapour deposition [6]. Most of these synthesis routes require high processing temperature for solid state kinetics [6] which are extremely challenging and expensive in case of bulk production. Therefore, solution-based processes are often preferentially chosen for conveniently controlling various process parameters [6].

In this study, co-precipitation method was followed that has been reported to have a significant control over particle size, shape, crystallinity, absorption efficiency and band gap of the nanoparticles with varying process parameters [6-7]. However, for favourable results, optimization of process parameters such as- precipitation temperature and pH, precursor and solvent type along with annealing conditions is of great significance [4]. The present experiment shows the importance of washing as a purification mechanism of nanoparticle preparation and how effectively through washing can improve structural properties of the manufactured nanoparticles. Increasing annealing temperature can also solve this

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issue, however, this results in increased crystallite size simultaneously.

2. Experimental Details

2.1 Materials

Zinc nitrate hexahydrate [$Zn(NO_3)_2.6H_2O$] (Sigma Aldrich) was used as precursor for the synthesis of ZnO nanoparticles. To control solution pH and as a precipitating agent, sodium hydroxide [NaOH] was added. Deionized water (DI) was used as the solvent as well as for washing the nanoparticles along with ethanol [C_2H_5OH].

2.2 CuO nanoparticle Synthesis

Pristine ZnO NPs were synthesized following co-precipitation route. Initially, 0.2M $Zn(NO_3)_2.6H_2O$ aqueous solution was prepared using DI water while stirring at 300 rpm. After dissolving, NaOH solution was added dropwise until pH value of the solution reached 7 and was kept settling down the precipitates overnight. Precipitates were collected by centrifuging the solution at 5000 rpm for 3 minutes, washed with DI water for several times and finally once with ethanol followed by drying at 120°C for 24 hours in an air oven. Later, after crushing and grinding, the dried powders were annealed at 450, 550 and 650°C for 2 hours heated at the rate of 5°C/min and finally, was cooled in the furnace. In a separate trial dried powder was vigorously rewashed and dried before annealing to remove the undesirable phase.

3. Characterization

3.1 X-Ray Diffraction (XRD) Analysis

XRD analysis was performed between 20 to 80° Bragg's angle and at a step rate of 2°/min using Bruker D8 Advance XRD Machine where Cu-$K_{\alpha 1}$ radiation of wavelength 1.5406Å was used as the source irradiation. The XRD spectra obtained by using OriginPro software revealed the structural orientation of the ZnO NPs. Highscore Plus software was used to perform Rietveld analysis of pure ZnO nanoparticles. Average crystallite size and percentage of crystallinity were calculated using Debye Scherrer equation and ratio of the integrated area of all crystalline peaks to the total integrated area under the XRD curve, respectively.

4. Results and Discussion

4.1 Presence of Unwanted Compound in Pristine ZnO NPs

Initially, pristine ZnO NPs were synthesized by annealing at 450°C, and analysis of the XRD pattern evidenced its hexagonal wurtzite crystal structure (Fig. 1). However, the analysis showed an additional peak at 29.4°, which was later identified to be present for Nitratine ($NaNO_3$), a nitrate salt, from Rietveld analysis.

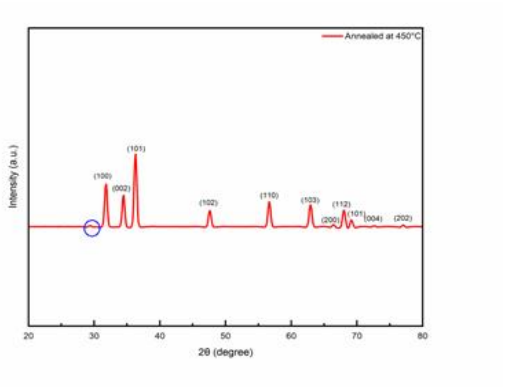

Fig 1: XRD pattern showing undesirable peak for pristine ZnO annealed at 450°C.

4.2 Undesirable Compound Formation During Precipitation

Nitratine ($NaNO_3$), the undesirable compound, is basically a nitrate salt, produced due to the reaction of $Zn(NO_3)_2.6H_2O$ with NaOH as following-

$$Zn(NO_3)_2.6H_2O\ (aq) + 2NaOH\ (aq) \rightarrow Zn(OH)_2 \downarrow (s) + 2\ NaNO_3\ (aq) + 6H_2O$$

Here, due to complete insolubility of $Zn(OH)_2$ in aqueous solution, it precipitates instantly. On the contrary, $NaNO_3$ formed in this reaction is highly soluble in water and therefore, it is presumed to get readily dissolved in the solution. However, in the XRD pattern, a major peak of this soluble salt was identified which can be attributed to the presence of $NaNO_3$ in the nanoparticles after washing (Fig. 1).
Two different approaches were attempted to remove the unwanted $NaNO_3$ compound. One was adequate washing of the $Zn(OH)_2$ precipitates prior to their drying. The other approach was to choose a higher annealing temperature, since, increasing annealing temperature usually leads to the thermal degradation of such unwanted compounds synthesized at the low precipitation temperature [8-9].

4.3 Removal of Unwanted Compound

To demonstrate the aforementioned presumption, unannealed ZnO NPs were rewashed for several times and dried again. XRD analysis revealed that this rewashing step led to the removal of several peaks that were present in the earlier XRD pattern of the unannealed powders (Fig. 2). It is observed that after rewashing and drying again, the peak intensities of the

wurtzite phase increased which can be attributed to the reduced scattering effect after removal of the unwanted compound.

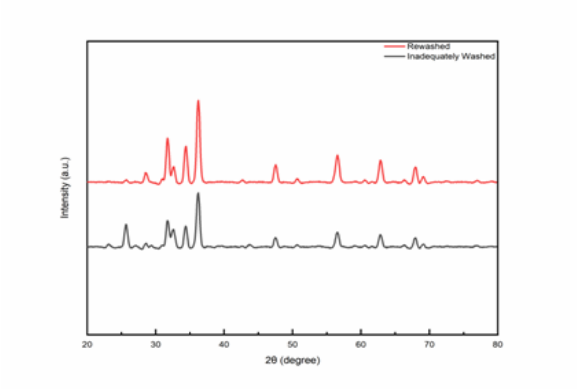

Fig 2: XRD pattern showing effect of rewashing.

To investigate the effect of increased annealing temperature, precipitates were annealed at 550 and 650ºC in addition to the prior annealing at 450ºC without rewashing (Fig. 3) The XRD results revealed that with increasing annealing temperatures, intensity of the undesirable peak observed earlier was mitigated and completely removed at 650ºC. This can be due to the decomposition of $NaNO_3$ at 650ºC, as this compound thermally decomposes above 600ºC [10]. Analysis of the XRD patterns showed an increase in crystallinity with increasing annealing temperature due to the higher thermal energy (Table 1) [11].

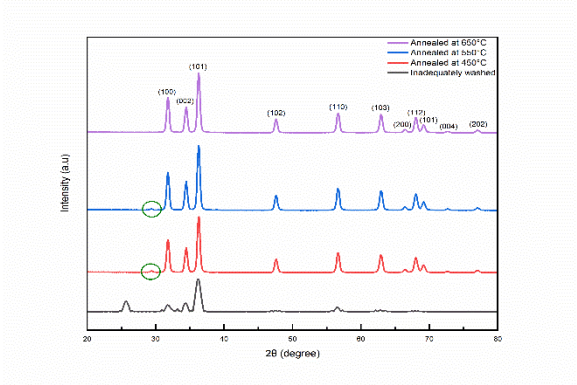

Fig 3: XRD pattern showing effect of annealing temperature without rewashing.

To investigate the effect of rewashing, precipitates were annealed at 450, 550 and 650ºC after rewashing (Fig. 4). XRD patterns revealed the removal of the $NaNO_3$ phase for any annealing temperature at or above 450ºC. Here as before, crystallinity was increased with increase in annealing temperature (Table 1) [12].

It can be affirmed that with increasing annealing temperature, both crystallinity and crystallite size of the pure ZnO nanoparticles increased since higher temperature can recrystallize the nanoparticles and therefore, reduce the effect of strain broadening [13].

Besides, inadequately washed pure ZnO nanoparticles showed lesser crystallinity compared to the rewashed nanoparticles since washing of nanoparticles enhance their structural properties noticeably.

It can be concluded from the XRD analysis that insufficient washing is the primary reason of the undesirable peak observed in the XRD patterns studied initially. Which implies, due to lack of adequate washing, $NaNO_3$ precipitates were present with the synthesized ZnO NPs even after their water-soluble nature. Rewashing can mostly eliminate the presence of such unwanted compounds. This finding seems to be of great importance since presence of unwanted peaks are often observed in nanoparticles synthesis process following co-precipitation method where in most cases the issues remained unnoticed and unexplained. In this study, it was also evident that increasing annealing temperature can lead to the thermal decomposition of such less thermally stable unwanted phases. However, from Table 1 it can be concluded that the rewashing is the better option since increasing annealing temperature results in increased crystallite size which is undesirable for most of the advanced functional applications.

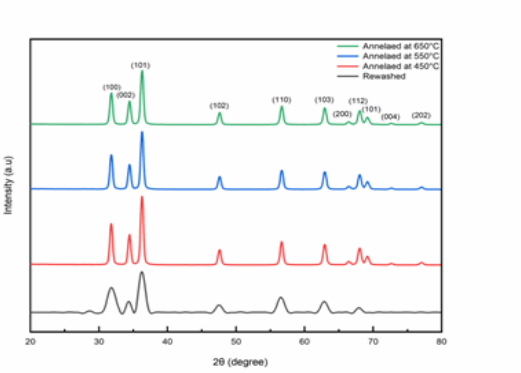

Fig 4: XRD pattern showing effect of annealing temperature after rewashing.

Table 1: Crystallographic data from XRD pattern analysis.

Annealing Temperature (ºC)	Percentage of Crystallinity (%)		Average Crystallite Size (nm)	
	Inadequately Washed	Vigorously Washed	Inadequately Washed	Vigorously Washed
450	91.77	93.54	19.67	19.59
550	93.79	94.27	21.40	20.67
650	94.83	95.17	22.14	21.83

5. Conclusions

Pure ZnO nanoparticles were synthesized using co-precipitation method. The nanoparticles showed an unwanted peak at 29.4° in the XRD pattern which was identified to be of Nitratine ($NaNO_3$) compound. Later it was confirmed that this nitrate salt was present due to the inadequate washing. After increasing annealing temperature at 650°C, this compound was thermally decomposed. In another attempt, annealing at even lower temperature of 450°C after rewashing results in the removal of this unwanted compound. Because of smaller crystallite size, the later approach was chosen as the preferable option.

6. References

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