Synthesis and characterization of ZnO nanostructures with varying morphology

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Abstract. Uniform fine particles of zinc oxide were prepared in three different morphologies and sizes by the controlled precipitation process from aqueous solutions of zinc nitrate in the presence of ethylene glycol. Ammonium hydroxide solution was used as the precipitant. Composition of the reactant solution, pH and temperature significantly affected the particle uniformity with respect to shape and size. Uniformity in the particles morphological feature was achieved under a narrow set of experimental conditions. pH of the reactant solutions and isoelectric point of zinc oxide were considered the master variables, controlling the particle size. One of the batch of the as-prepared zinc oxide particles was calcined at 750°C, which increased its crystallinity, changed its various lattice parameters, Zn–O bond length and preferred orientation of the crystal *hkl* planes. Calcination had little effect on the original morphology of the zinc oxide particles.

Keywords. Zinc oxide; uniform particles; precipitation; preferred orientation; texture coefficient.

1. Introduction

Zinc oxide (ZnO), a material of considerable interest, offers striking benefits in biomedical and clinical sites owing to its distinguished performance and novel applications. ZnO has been proved a boon for researchers due to its superb properties like effective antimicrobial activity, nontoxicity and biosafety [1]. ZnO has a remarkable history of multidimensional and safe uses and may be considered as one of the most applied drugs of all times. ZnO is an excellent UV filter and is extensively used in cosmetics. It is, particularly, used in sunblock due to the broad spectrum of UV radiation absorption, superior transparency, high photostability and biocompatibility [2]. In addition, ZnO is very useful to cure various other skin ailments, e.g., in products like antiseptic ointments, antidandruff shampoos, etc., reflecting its antifungal and antibacterial actions. One of the foremost attributes of ZnO nanoparticles is ZnO tape, available in the market and used as bandage by athletes to prevent damage of soft tissues [3]. ZnO has been accepted by ‘World Union of Wound Healing Societies’ in 2004 in Paris, for having the potential of wound healing as it accelerates the healing process once it is applied on wounds [4,5]. A comparative study revealed that ZnO stayed more effective for treating burn wounds and dermis maturation as compared to other compounds, such as silver sulphadiazine [6]. Recent findings indicated that ZnO could be used as promising candidate for coating of orthopedic as well as dental implants, due to its remarkable antimicrobial activity [7]. For instance, ZnO is one of the primary

components in dental prosthetics and is employed in the form of zinc oxide eugenol base, a well-known, suitable and effective choice for filling dental cavities [8]. Moreover, ZnO in composite form with anticancer drug doxorubicin called as Dox–ZnO nanocomplex has been regarded as a promising agent for inclusive cancer treatment [9,10].

Hence, ZnO can be considered as a magic material due to such broad-spectrum applications as well as flexibility of fabrication in diverse morphologies. As such, most of the researchers have employed commercially available ZnO, while others have synthesized it through different techniques. However, several studies have shown that particle shape, size and uniformity profoundly affected the properties and performance of ZnO nanoparticles. Talebian *et al* [11] reported that particle morphology significantly affected the antibacterial activity of ZnO nanoparticles. Therefore, control over the particle morphology, size, as well as uniformity is the most basic requirement for its biomedical uses [12–14]. Most of the researchers succeeded in synthesizing ZnO nanoparticles with reasonable uniformity in particles’ architecture, but they employed either complicated and time-taking procedures or sophisticated instrumentation, which is the major hindrance in applying these methodologies in actual practices.

In the present study, we have developed simple, time-effective and economically feasible method for the synthesis of uniform fine particles of ZnO in different novel shapes and sizes that could be more suitable for the wide range of medical applications. For this purpose, we have selected aqueous solutions of zinc nitrate, ethylene glycol and ammonia

as precursors and in addition explored the effect of different synthesis parameters; i.e., composition of reactant mixture, temperature and pH on particles morphological characteristics. We have selected zinc nitrate and ammonia because (i) zinc is nutritionally one of the most essential element and is present in human body tissues [15], (ii) nitrate comes in the human body from plant-based diet, gets transformed into nitric oxide that reduces hypertension and (iii) ammonia is also found in the human body and plays a key role in body's protein synthesis, nitrogen cycle as well as maintains the pH balance of the body.

2. Experimental

2.1 Materials

Reagent-grade zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), ethylene glycol ($\text{C}_2\text{H}_6\text{O}_2$), ethanol ($\text{C}_2\text{H}_5\text{OH}$) and ammonium hydroxide (25%, NH_4OH solution) were purchased from Scharlau and used without further purification. All the stock and working solutions were prepared in double-distilled water, and Pyrex glassware was used throughout the experimental work. Membrane filter papers of pore size $\sim 0.2 \mu\text{m}$ were used for filtration process.

2.2 Synthesis of ZnO particles

ZnO particles were synthesized by heating aqueous solutions, containing zinc nitrate hexahydrate ($1.5\text{--}5 \text{ mol l}^{-1}$), ethylene glycol ($1\text{--}15 \text{ mol l}^{-1}$) and ammonium hydroxide (1–15%), at various temperatures ($30\text{--}90^\circ\text{C}$), for known intervals of time (5–30 min) in the thermostatic water bath. The resulting precipitates were then isolated from the mother solutions by vacuum filtration, washed thoroughly with deionized water and then with ethanol to completely remove the remnants of mother liquor. Finally, the obtained residues were allowed to dry at room temperature, and then stored in a desiccator for further use.

2.3 Heat treatment

Pre-weighed powder sample of the selected batch of the synthesized particles was heated in a furnace (Nabertherm L5/11/B180, Germany) up to 750°C at the heating rate of $10^\circ\text{C min}^{-1}$. The sample was kept inside the furnace at the mentioned temperature for 2 h. The furnace was then turned off, and the sample was allowed to cool down to room temperature inside the furnace. The heat-treated sample was then removed from the furnace, and weighed again, in order to determine the weight loss occurred during the heat treatment. It was then stored in a tightly stoppered glass bottle.

2.4 Characterization

2.4a Scanning electron microscopy: Morphology of the particles was inspected using scanning electron microscope

(SEM; JEOL, JSM-5910, Japan). For this purpose, a small quantity of the desired sample was mounted over the standard aluminium stub through the double stick conducting carbon-tape and then coated with gold for 40 s in an auto-fine coater (JEOL, JFC-1600). The gold-coated sample was then shifted to the vacuum chamber of the SEM and the images were obtained through the standard procedure.

2.4b Fourier transform infrared spectrometry: Infra-red spectroscopic analysis of the desired powder samples was performed with the Fourier transform infrared (FTIR) spectrometer (Schimadzu, FTIR-8400S, IR Prestige-21). In each analysis, small amount of the powder sample was thoroughly mixed with IR-grade potassium bromide and then placed in the sample holder of the Diffuse Reflectance Accessory (DRS-8000A), assembled in the same machine. Each of the samples was scanned 10 times from 4000 to 400 cm^{-1} .

2.4c X-ray diffractometry: In order to assess the crystallinity of the desired powder samples, X-ray diffractometry (XRD) patterns of the latter were recorded with the X-ray diffractometer (JEOL XRD, JDX-3532) by using $\text{Cu-K}\alpha$ radiations. The scanning was performed in the 2θ range of $5^\circ\text{--}80^\circ$ and the step angle was kept at 0.05° . During scanning, the applied current and accelerating voltage used were adjusted to 20 mA and 40 kV, respectively.

2.4d Thermogravimetric/differential thermal analysis: Thermal analysis of the selected powder sample was carried out with a simultaneous thermogravimetric/differential thermal analysis (TG/DTA) analyzer (Diamond TG/DTA, Perkin Elmer). Heating was performed in the air atmosphere at the rate of $10^\circ\text{C min}^{-1}$.

3. Results and discussions

3.1 Synthesis

Precipitated particles of zinc oxide in different shapes and sizes were produced by bubbling ammonia gas through aqueous solutions of zinc nitrate and ethylene glycol for various periods of time at different temperatures. In all cases, precipitated solids formed in the reactant mixtures. The precipitation reaction essentially emerged because of the reaction of ammonia with the dissolved zinc ions in aqueous medium according to the following reactions [16]:

SEM analysis of the precipitated solids revealed that most of them composed of particles in irregular morphologies in

Figure 1. SEM images of the ZnO particles obtained by heating reactant solutions of different pH values, containing appropriate amounts of zinc nitrate, ethylene glycol and ammonium hydroxide, at 80°C for 15 min. Particles in **a–c** were produced in solutions, adjusted to pH 5.41, 8.01 and 9.69, respectively.

the form of either discrete particles or embedded material in the gelatinous matrix. These results showed that, the precipitation conditions and composition of the reactant mixtures had a significant effect on the morphology of the precipitated particles. As such, the applied experimental conditions were optimized with respect to the composition and the stirring rate of the reactant solutions, flow rate of the ammonia gas, temperature and pH in order to acquire shape and size uniformity in the precipitated particles. Following these optimization trials, it was noted that the particles of uniform shape and size were produced under a narrow set of experimental conditions.

Figure 1 exemplifies the SEM images of particles obtained under the given experimental conditions. XRD studies demonstrated that all the three batches of the displayed particles were crystalline in nature and had identical XRD profiles. The latter were analysed with the help of a software (JDX-3532), which identified the tested materials as polycrystalline ZnO (card no: ICCD-50664) of hexagonal phase with the lattice constants $a = b = 0.3249$ nm, and $c = 0.5205$ nm.

Inspection of the images in figure 1 revealed that increase in pH of the reaction medium resulted in the increase in particle size, which was also accompanied by the change in particle morphology. In order to account for the effect of pH on the observed results, we believe that pH of the mother liquor of the smaller particles (SEM, figure 1a) was well below the isoelectric point ($\text{pH}_{\text{iep}} \sim 9.56$) of the zinc oxide [17,18]. Under

such conditions, the formed particles were highly positively charged, which in turn inhibited their expected homocoagulation and thus stayed smaller. With the increase in pH of the reactant mixture to 6.7, the positive surface charge density on the precipitated particles decreased, which facilitated the homocoagulation of the formed particles and thus the full-grown particles attained a larger size (SEM, figure 1b). In addition, the increase in pH of the medium also appears in the form of a shape-directing parameter for the particles in the present system, as each of the full-grown particles acquired the shape of a sunflower (SEM inset, figure 1b). To our knowledge, such type of pH-dependent observation has never been reported before. Similarly, further increase in pH to 9.06 resulted in larger particles, which was obviously due to the effective homocoagulation of the precipitated particles. Morphology of the particles in figure 1c also suggested the fact that under the mentioned pH, initially the sunflower-shaped particles formed which then merely coagulated together and produced large-size particles. Schematic illustration of the change in particle morphology is presented in figure 2. Other researchers [19–23] also produced particles of zinc oxide by chemical precipitation process from zinc salt solutions; however, most of them employed surfactants and rather time-consuming and relatively uneconomical methods than those reported in this work. We believe that due to uniformity in particle shape and size as well as their novel morphologies,

Figure 2. Schematic illustration of the change in particle morphology of ZnO particles with pH.

Figure 3. (a) DTA and (b) TGA curves obtained for particles displayed in figure 1a.

the zinc oxide particles, shown in figure 1, would perform effectively in various biomedical applications [6–10] in a reproducible manner. It is added that the particles shown in figure 1b were selected for further study in this work and will be designated as ZnO_{ap} in further discussion.

3.2 Thermogravimetry

In order to explore the effect of temperature on the properties of the ZnO_{ap} particles, the latter were heated in the temperature range of 30–800°C in the TG/DTA analyser and the obtained thermal profile is displayed in figure 3a. This figure showed that the tested sample lost its weight in three distinct steps in the temperature range, 30–350°C. The first weight loss took place at once when heating started, i.e., at about 30°C; second one at 55°C; whereas the third weight loss started at around 100°C. The total weight loss observed was about 6.87%, which was due to the loss of the surface adsorbed water molecules. Over this temperature range, the weight of the sample stayed nearly unaffected by the increase in temperature. This observation showed that the tested material possessed no other components, except water, which

could be thermally, decomposed up to heating at 800°C. The experimentally determined weight loss (6.87%) was in good agreement with the one estimated theoretically (i.e., 6.864%) through the following reaction (Eq. 3):

Similarly, the corresponding DTA trace (figure 3b) recorded simultaneously with the TGA data in the same plot showed no prominent peak associated with exo/endothermic nature of the thermal weight loss reaction occurred during the TGA experiment. This indicated that the association of the water molecules with the ZnO_{ap} particles was purely physical in nature. Other researchers also observed such type of behaviour during the heat treatment of the ZnO particles, synthesized by the other routes [24].

Using the TGA data (figure 3a), the activation energies associated with the observed weight losses from the ZnO_{ap} powders during the three weight loss steps (pointed in the same figure) were estimated by means of a well-known Coats Redfern equation (Eq. 4) [25,26].

$$\ln[-\ln(1 - \alpha/T^2)] = -E_a/RT - \ln[(AR/\beta E)(1 - (2RT/E))], \quad (4)$$

where β is heating rate, $\ln[(AR/\beta E)(1 - (2RT/E))]$ is constant, R is universal gas constant, T the temperature and α the fractional decomposed mass of the original material. By plotting the TGA data in terms of $\ln[-\ln(1 - \alpha/T^2)]$ against $1/T$ for the three weight loss steps, activation energies were calculated by using Eq. 4 and are given in table 1. As can be observed from this table, the calculated values of activation energy for all the three steps are nearly the same, which indicated that the thermally induced weight losses in the observed three steps were due to the desorption of surface water with no associated phase change in the solid matrix.

Based on the information about the response of the ZnO_{ap} particles towards the temperature, obtained from the TGA data in figure 3a, another experiment was performed in which

Table 1. Thermal weight losses and corresponding activation energies estimated for ZnO particles shown in figure 1b.

Temperature (°C)	Weight loss (%)		E_a (kJ mol ⁻¹)
	Experimental	Theoretical	
30–36	6.87	6.864	0.665
55–68			0.633
100–350			0.807

Figure 4. Scanning electron micrograph of the ZnO_{cal} particles.

rather larger amount of the ZnO_{ap} powder was calcined in a furnace at 750°C under controlled heating rate (5°C min⁻¹). SEM image (figure 4) of the calcined ZnO particles (to be designated as ZnO_{cal}) revealed that the thermal weight losses slightly affected morphology of the ZnO particles.

3.3 Infrared spectrometry

The purity and composition of the ZnO_{ap} particles were also ascertained by the infrared spectrometry. Figure 5a depicts the FTIR spectrum of these particles, obtained in the range 400 to 4000 cm⁻¹. As can be seen, the spectrum consisted of several absorption bands, located at different frequencies, which were obviously due to the vibrational modes of different groups present on the surface of these particles. To be more specific, the broad absorption bands, centered at 3438 and 2075 cm⁻¹ were due to the stretching vibrations of the O–H group of the surface adsorbed water; the absorption band positioned at 1627 cm⁻¹ was attributed to the bending modes of vibration of the O–H group. Similarly, the absorption bands appeared in the finger print region at 1387 and 896 cm⁻¹ were indicative of the stretching vibrational modes of nitrate (NO₃⁻) ions, possibly inherited by ZnO_{ap} particles from the zinc nitrate solution during the precipitation process. Likewise, a relatively more intense and broad band was observed in the region of 526–427 cm⁻¹, which represented the characteristic stretching vibration mode of Zn–O bond.

Similarly, FTIR profile (figure 5b) of the ZnO_{cal} particles revealed that in comparison with the ZnO_{ap}, the intensity of

Figure 5. Fourier transform infrared spectrum of the (a) ZnO_{ap} and (b) ZnO_{cal} particles. **Figure 6.** X-ray diffraction pattern of the (a) ZnO_{ap} and (b) ZnO_{cal} particles.

the absorption bands corresponding to O–H stretching and bending vibrations at 3449, 2346, 1628, 1518 cm⁻¹ reduced, while the band at 896 cm⁻¹, ascribed to the remnant NO₃⁻ ions, almost diminished. The observed changes in the spectrum of the ZnO_{cal} were obviously due to the loss of water molecules from the solid surface and the decomposition of the nitrate ions during the calcination process. Additionally, the intensity of the Zn–O characteristic absorption band at 536–427 cm⁻¹ became more prominent, showing the increase in purity of the ZnO_{cal} particles.

3.4 X-ray diffractometry

Figure 6a exemplifies the XRD pattern of the ZnO_{ap} particles, in which the intensity of the diffracted data was recorded

Table 2. Average crystallite size and other related parameters of ZnO_{ap} and ZnO_{cal} particles.

Material	Peak	FWHM (°)	2θ (°)	Crystallite size (nm)	Average crystallite size (nm)
ZnO _{ap}	1st	0.929	31.757	8.61	9.95
	2nd	0.863	34.372	9.30	
	3rd	0.673	36.208	11.95	
ZnO _{cal}	1st	0.555	31.804	13.20	13.45
	2nd	0.599	34.472	13.45	
	3rd	0.589	36.285	13.70	

over 2θ range of 10–80. As can be seen, the displayed XRD pattern is composed of diffraction peaks at 2θ positions of 31.776°, 34.468°, 36.281°, 47.582°, 56.603°, 62.924° and 66.447°, which corresponded to reflections from different crystal planes, i.e., (100), (002), (101), (102), (110), (103) and (200), respectively. No additional peaks characteristic of other crystalline phases or impurities appeared in the displayed XRD pattern, which confirmed that the ZnO_{ap} was composed of zinc oxide. It is worth mentioning that the XRD pattern observed for the mentioned product matched well with those reported elsewhere [27,28], which pointed to the fact that the synthesis route did not affect the bulk characteristics of ZnO_{ap} in the present findings.

Similarly, the XRD profile (figure 6b) of the ZnO_{cal} consisted of sharp peaks at the same 2θ positions, as appeared in the XRD pattern (figure 6a) of the ZnO_{ap} particles, which revealed that the heat treatment at the described temperature had negligible effect on the crystal phase changes. As such, the data of the three major peaks in the XRD patterns of both ZnO_{ap} and ZnO_{cal} powders were employed for the estimation of their crystallite sizes. The Debye Scherrer equation (Eq. 5) [24] was used for this purpose and the calculated crystallite sizes are given in table 2.

$$D = K\lambda/\beta \cdot \cos\theta \quad (5)$$

where D is crystallite size, K the Scherrer constant (0.94), λ the X-ray wavelength, β the full-width at half-maximum (FWHM) and θ the Bragg angle.

The FWHM values of the three peaks in the XRD patterns of the ZnO_{ap} and ZnO_{cal}, corresponding to (100), (002) and (101) planes, have been included in table 2. As can be noted, the FWHM values of the three peaks of the ZnO_{ap} decreased in order (100) > (002) > (101). In contrast, the FWHM values of the same peaks of the ZnO_{cal} remained almost constant. This observation revealed that the crystallite shape of the ZnO_{ap} was rather asymmetric, which attained obvious symmetry during the calcination process in the ZnO_{cal}. Similarly, the average crystalline size of the ZnO_{cal} was bigger than that of the ZnO_{ap}, which showed increased crystallinity in the ZnO_{cal}.

In addition, the inter- and intra-variations in the intensity of the diffraction peaks, corresponding to (100), (002) and (101)

Figure 7. Values of the texture coefficients of (100), (002) and (101) crystal planes in ZnO_{ap} and ZnO_{cal} particles.

planes in the XRD patterns of ZnO_{ap} and ZnO_{cal}, in figure 6, indicated preferred orientation of the mentioned planes. In order to assess quantitatively the degree of the preferred orientation, the values of texture coefficients were calculated for the mentioned three planes according to the following relation (Eq. 6) [29,30]:

$$TC_{(hkl)} = \left(\frac{I_{m(hkl)}}{I_{o(hkl)}} \right) / \left[\frac{1}{N} \sum_1^N \left(\frac{I_{m(hkl)}}{I_{o(hkl)}} \right) \right], \quad (6)$$

where, $I_{m(hkl)}$ and $I_{o(hkl)}$ are the measured and standard intensity (ICCD card no: 50664) of the hkl plane, and N is the number of the peaks selected for the estimation of the $TC_{(hkl)}$ values, which in the present case is equal to 3. The obtained $TC_{(hkl)}$ values are plotted in figure 7, which clearly showed that in ZnO_{ap} (002) plane was the preferred orientation of the crystallites, whereas it changed to (101) in the ZnO_{cal}. It is worth mentioning [31] that the value of $TC_{(hkl)}$ higher than 1 indicate the abundance of crystallites oriented in a given (hkl) direction, while the values $0 < TC_{(hkl)} < 1$ show the lack of crystallites oriented in that direction.

The lattice parameters (a and c) were also calculated for the ZnO_{ap} and ZnO_{cal} from the peaks (100) and (002) in their

Table 3. Various crystallographic parameters of ZnO_{ap}, ZnO_{cal} and ZnO_{standard} (ICCD: 50664).

Material	<i>a</i>	<i>c</i>	<i>c/a</i>	Unit cell vol. (nm ³)	Zn–O bond length (nm)
ZnO _{ap}	0.3256	0.5213	1.60093	0.04786	0.19812
ZnO _{cal}	0.3248	0.5205	1.60254	0.04755	0.19767
ZnO _{standard} (ICCD: 50664)	0.3250	0.5207	1.60215	0.04763	0.19776

XRD patterns (figure 6a, b) by using the following relations (Eqs. 7 and 8) [32]:

$$a = \lambda / (\sqrt{3} \sin \theta) \quad (7)$$

$$c = \lambda / \sin \theta \quad (8)$$

In addition, the length (*L*) of the Zn–O bond in these two solids was estimated by the following formula (Eq. 9) [33]:

$$L = \sqrt{(a^2/3) + (0.5 - u)^2 c^2}, \quad (9)$$

where, *u* for the hexagonal structure was calculated by Eq. 10 [33].

$$u = (a^2/3c^2) + 0.25 \quad (10)$$

Similarly, the unit cell volumes (*V*) of the same two samples (ZnO_{ap} and ZnO_{cal}) were calculated by using Eq. 11 [33].

$$V(\text{nm}^3) = 0.866 \times a^2 \times c \quad (11)$$

All the above-mentioned calculated parameters are presented in table 3. As can be observed, the values of *a* and *c* for ZnO_{cal} are much closer to the values of the same parameters for the ZnO_{standard} (as per ICCD-50664) as compared to that of ZnO_{ap}. This indicated relatively high crystallinity of ZnO_{cal}. Similarly, the value of the *c/a* parameter of ZnO_{cal} also showed good match with that of the ZnO_{standard}. Additionally, the values of unit cell volume and Zn–O bond length of the ZnO_{cal} were also found closer to ZnO_{standard}, which revealed that calcination transformed ZnO_{ap} into solid of high-quality crystallinity (ZnO_{cal}).

4. Conclusions

- Uniform particles of ZnO in different shapes and sizes were precipitated from zinc nitrate solution in the presence of ethylene glycol with ammonium hydroxide.
- Uniformity of the precipitated particles with respect to morphology and size was dependent upon the composition of the reactant mixture, temperature and pH in a sensitive manner. Monodispersed particles were produced under a narrow set of experimental conditions.

- pH of the reactant mixture and isoelectric point of the ZnO played a major role in the finished architecture of the precipitated particles.
- The as-prepared ZnO particles were crystalline and contained some water, which was removed by the heat treatment at the elevated temperature.
- Calcination at 750°C improved the crystallinity of the as-prepared ZnO, improved the crystallite symmetry and brought the crystallographic parameters closer to the standard values, described in the relevant ICCD card no: 50664.
- In addition, the heat treatment also changed the preferred orientation of the crystallite from the plane (002) in the as-prepared ZnO to the plane (101) in the calcined ZnO.

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