Effect of stirring time on ZnO nanoparticles properties and morphology

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Abstract. The impact of stirring time on the ZnO nanoparticles assembly and properties as a novel study was investigated. A precipitation technique has been used for synthesizing ZnO nanoparticles and the impact of stirring time as well as calcination temperature and time were analyzed. X-ray diffraction (XRD), field emission scanning electron microscopy (FE-SEM) and Fourier-transform infrared spectroscopy (FTIR) were used for characterizing the resulting powder. The effect of stirring time, (viz., 0, 2, 4 and 6 h), on the optical properties was investigated using UV-Visible spectroscopy. The XRD analysis shown that all of the acquired powders had a pure form of ZnO nanoparticles with distinct crystallite size. The best circumstances for ZnO nanoparticle synthesis were 2h stirrings time and 400°C for 1 h, as calcination temperature and time, respectively. The FTIR spectra show that ZnO nanoparticles prepared at different stirring times appeared in wavenumber range 435.3 - 458.2 cm⁻¹. SEM pictures reveal different surface distribution with some agglomeration through a variation on stirring time. The bandgap value was identical for 2 and 4 h stirring time with value 3.18 eV while, zero and 6 h stirring showing the same value with slight increase compared with 2 and 4 stirring to be 3.2 eV.

1. Introduction

The multifunctional and morphology ZnO nanoparticles attract many considerations nowadays due to its activity, high binding energy exciton (60 meV) and wide band-gap (3.37 eV) [1]. It is conscious to visible light [2, 3]; nonhazardous material for humans and animals and antibacterial agents because it is resistant to hard processing conditions [4]. Likened to organic materials, inorganic materials like ZnO have excellent thermal stability, greater durability, heat resistance and selectivity [5]. These assets have lead to numerous applications of ZnO in various technological areas, such as gas sensors, photocatalyst, catalysts, varistors, piezoelectric devices, ultraviolet photodiodes, field-emission displays, surface acoustic wave devices, medical and dental materials, sunscreens, rubber, coatings, pigments, concrete, ceramic, optoelectronics, industry, cosmetology, solar cells and cellulose fibers [6-17].

In ZnO nanoparticles synthesis, several synthesis techniques have been used in a pure form with different morphology and crystallite size. Midst the most mentioned techniques are aerosol process [18], sonochemical [19], microemulsions [20], mechanochemical process [21], vapor-liquid-solid growth [22, 23] vapor-phase transport [24, 25], template-assisted systems and vapor-phase epitaxy that extraordinary temperature methods, sol-gel [7], direct and hydrothermal precipitation [26] and spray pyrolysis [27].
Nevertheless, to accomplish the ultimate structure, these approaches usually require multiple stages, complex equipment and high temperature. Of these, the precipitation technique was designated for synthesis ZnO nanoparticles in this study. It is a friendly method, cost-effective, low temperature and forms numerous nanostructures [28, 29].

In supreme synthesis techniques, some variables should be measured and its effect of each on the final product was investigated. For precipitation technique, many parameters as calcination temperature and pH on ZnO nanoparticles size and properties were intensively considered, but the effect of reaction stirring time not considered in literatures till now. The objective of this paper is to synthesize ZnO nanoparticles in pure form and to investigate of the impact of the time-stirring on its optical feature and morphology.

2. Experimental

2.1. Materials
For the preparation of zinc oxide Nanoparticles, zinc acetate and NaOH were used of analytical grade (sigma-Alderich) without further purification.

2.2. Synthesis of ZnO nano powder.
Firstly, sodium hydroxide solution (2 M) was added to zinc acetate solution (1 M) with constant stirring for diverse stirring time (0-6 h). The resulted white precipitate was filtered off and washed several times with deionized water, then the obtained precipitate was dried at 100 °C. Finally, the resulting powder calcined at different temperature 300 °C-600 °C for different interval times 0.5-4 h.

2.3. Characterization
The resulted powders characterization was set by X-ray diffraction (XRD) BrukerAXSD8 Germany Cu Kα radiation 0.154. FTIR analysis was done by an Agilent Technologies, Cary 630. Field Emission-Scanning Electron Microscopy (FE-SEM) was achieved using (FE-SEM, QUANTAFEG250, Netherlands). Bandgap characterization was done using Jasco V-670 spectrophotometer (ISN-723, Japan).

3. Result and discussion

3.1. XRD Analysis

3.1.1. Effect of calcination temperature. Calcination impact on the ZnO nanoparticles synthesis is an important parameter since it indicates the stability of the substance and its temperature of crystallization. This effect was studied in the range of 100-600°C. As indicated from figure 1, high intensity and complete crystallization of ZnO nanoparticles was obtained at 400°C. As observed from the previous literature and the TGA analysis, the precursor can be completely decomposed to ZnO after annealing at ~ 350°C[16, 30]; whereas, Moharram, et al., found that, the mass leakage ends at about 300 °C which is due to the decomposition of Zn(OH)₂. The best improvement of the ZnO NPs after calcination process was at 400°C[31].

The Debye–Scherer approach has been used for considering ZnO nano crystallite size as set out in Eq.(1). Varying calcination temperature resulted in a distinction of the ZnO size. It was observed that, decrease in crystallite size from 82.4 nm to 44.1 nm was obtained with scaling up calcination temperature (100-300°C). Further rise in calcined temperature to 600°C, drastically growth in crystallite size was observed. Reduction in crystallite size at low calcined temperature is revealing of the reorganization process; while at calcination temperature >300°C increase in crystallite size is revealing of reinforcement of ZnO phase [32].
where, $D$, $\lambda$, $\beta$ and $\Theta$ are crystallite size, X-ray source wavelength, the full width at half maximum of the peak and the angle at which diffraction intensity is maximized. From the study it was observed that, the color of obtaining ZnO powder is yellow, which returned to white with cooling. This phenomenon explained by the fact that, ZnO exhibits a thermochromism property wherein it changes its color with increasing temperature. This is probably because of the loss of oxygen which results in the formation of crystal lattice defects [5, 33].

![Figure 1. Effect of calcination temperature on the synthesis of ZnO nanopowder at 100, 300, 400, 500 and 600°C.](image1)

![Figure 2. Effect of stirring times on the synthesis of ZnO nanopowder at no stirring, (2 h), (4 h) and (6 h).](image2)

3.1.2. Effect of stirring time. The stirring time was analyzed in the range 0-6 h. It was found that all reaction times lead to the pure ZnO formation with different intensity and crystallite size with no second phases appeared. The greatest stirring time is 2 h, as illustrated in figure 2 with the maximum peak intensity and the smallest crystallite size compared with other stirring times. The peaks FWHM increases as stirring time increases. At zero time, figure 3, stirring, the high crystallite size (148 nm) was observed of ZnO nanoparticles as a result of the insufficient distribution of small particles leading to accumulation. At 2 h stirring time, high crystallization with small 74 nm crystallite size was obtained. With increasing stirring time crystallite size augmented. This may explain as small particles acquired energy from the stirring process leading to an increase in the collision rate. Consequently, the combination of small particles into larger particles and hence aggregation resulted in the grain size enlarges [34, 35]. Surabhi Siva Kumar, et al., [16] synthesized nano ZnO for 12 h in dynamic stirring.

3.1.3. Effect of calcination time. Calcination time was varied in the range 0.5-4 h. From XRD pattern, figure 4, it was clear that, as calcination time increased the peak intensity and crystallite size gradually increased to be maxima at 4h. Not any diffraction peaks of second phases were perceived. At the short time, (0.5h), high intensity and 123nm crystallization size was obtained. The phenomenon of scale up crystallite size with calcination time qualified to the growth of the crystalline volume to the surface ratio, which happened due to particle size enlargement [36].
3.2. FE-SEM analysis

The stirring periods impact on the ZnO nano powder morphology has been evaluated by mean of the field emission scanning electron microscope (FE-SEM). The FE-SEM images of nano ZnO with stirring time: zero, 2, 4 and 6 h were represented figures 5. All images demonstrate spherical natures at high magnification level with particle size in nano scale (smaller than 100 nm).

At high magnification, spherical shapes were observed for all stirring times as illustrated from figure 5(a, c, e, g) with a tendency of agglomeration growth for zero and 6 h stirring times. Some spherical cages (raspberry-like) for 4 h stirring time appeared. The particle size was found to be 20-92, 25-46, 32-72 and 45-82 nm for zero, 2, 4 and 6 h stirring times, respectively. At low magnification, the surface topography was diverse with respect to stirring time. For zero time, figure 5(b), some plate-like morphology appeared plus the spherical particles, whereas the surface is a flat and the well-ordered morphology in the form of a flake-like identity with uniform surface topography was obtained in case of 2 h stirring as shown in figure 5(d). No agglomeration appeared was obtained. Stirring for 4 h, figure 5(f), gives surface morphology of a sponge-like shape. Irregular platelets also observed. The structure for 6 h stirring appeared in figure 5(h) many agglomerations and the particle arranged to form a sheet-like surface.

3.3. FT-IR analysis

Figure 6 exemplifies the FTIR bands of the produced nano ZnO, stirred at zero, 2, 4, and 6 h. The synthesized ZnO nanoparticles peaks were observed between 435.3 and 458.2 cm⁻¹ [37, 38]. The peak area scaled up as stirring time increased, indicating increasing crystallite size. The C=O stretching was observed for all stirring times between 1622 until 1634 cm⁻¹ [39], which gradually increased with increasing stirring time. Peaks related to O-H were observed in 3435 cm⁻¹ [40] which diminished regularly as stirring time raised. This may relate to the more consuming OH⁻ reacted with zinc salt as time increased [41].

3.4. Optical properties

By measuring the diffuse spectroscopy of reflectance, the clarification of optical properties was achieved. The diffuse reflectance (R) was considered against wavelength as displayed in figure 7 for the altered stirring times of ZnO. The spectra were done in the wavelength range 200-1200 nm. The bandgap was calculated using the Kubelka-Munk function F(R) given in Eq. (2) [1, 42]. The gap energy was estimated through drawing the F(Rhv)² Kubelka-Munk function versus energy (hv) as exhibited in figure 8. The straight line
Figure 5. Effect of stirring times on the morphology of ZnO nanopowder at stirring time: (a,b) zero, (c,d) 2, (e,f) 4 and (g,h) 6h at high (2 μm) and low (10 μm) magnification.
Figure 6. FT-IR spectrum of ZnO nanoparticle synthesis at stirring time 0, 2, 4 and 6h.

The difference in gap energy values associated with the variation in particle size, morphologies and the agglomeration formation of the nano ZnO [43]. For zero and 6 h stirring time, high particle size compared to 2 and 4 h stirring time, it has been observed that the bandgap for zero and 6 h stirring are higher than other stirring time. The slight difference in band gap is related to structural variation and the appearance of some agglomerations which resulted from alteration of stirring times [1, 41]. Previous literature determined bandgap of ZnO nanoparticle to be 3.41 eV[32], 3.63 eV[44], 3.10-3.37eV [45], and 3.35 eV [46].

4. Conclusion

Nano ZnO was well prepared under numerous synthesis conditions through the precipitation process. The XRD and the FTIR confirm the great crystalline and pure form of nano ZnO nanoparticles in each synthesized powder. The particle size relies on calcined temperature and time. It crystallized with scaling
up the calcination temperature as well as time. Nano ZnO synthesis at 400 °C for 1 h calcination time and 2 h stirring time show the best feature and minimum crystallite and particle size. The stirring period influence on the structure and optical feature of prepared nano ZnO. Spherical assembly with a variety of particle sizes was found whereas, the surface organization for each stirring time was different. The bandgap increase from 3.18 to 3.2 ev with stirring time increment from 2 to 6 h.

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