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Article

Room Temperature syntheses of ZnO and its structure

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Abstract: ZnO has many technological applications which largely depend on its properties that can be tuned by controlled synthesis. Ideally, the most convenient ZnO synthesis is carried out at room temperature in aqueous solvent. However, the correct temperature values are often loosely defined. In the current paper we performed synthesis of ZnO in aqueous solvent, by varying reaction and drying temperature by 10°C steps and monitored the synthesis products primarily by XRD. We found out that a simple direct synthesis of ZnO, without additional surfactant, pumping of freezing, required both a reaction (T_P) and a drying (T_D) temperature of 40°C. Higher temperatures also afford ZnO, but lowering any of the T_P or T_D below the threshold value results either in the achievement of $Zn(OH)_2$ or in a mixture of $Zn(OH)_2$/ZnO. A more detailed Rietveld analysis of the ZnO samples reveals a density variation with the synthesis temperature and an increase of the nanoparticles average size also verified by SEM images. The optical properties of ZnO obtained by UV-Vis reflectance spectroscopy indicate a red shift of the band gap by ~0.1 eV.

Keywords: ZnO; Room Temperature Synthesis; XRD Characterization UV-Vis reflectance spectroscopy

1. Introduction

Metal and mixed metal and semiconductor oxides are widely applied in several fields, as supercapacitors [1,2,3], gas sensors based on chemoresistivity [4,5,6,7,8], or by using dielectric excitation [9,10], heterojunctions [11,12], energy storage as in batteries [13-15], and electrochemistry [16-18]. Their properties can be varied in different ways, by doping [19], capping, and controlling structure, shape and size, with bottom-up and top- down approaches [20-27]. Types of synthesis include sol-gel methods, hydrothermal synthesis, solvothermal synthesis, electrospinning [28-34]. Among the oxides, ZnO has been thoroughly investigated because of its properties, such as a wide band gap (~3.35 eV) with a high exciton binding energy of (~60 meV), wurtzite crystal structure, piezoelectric properties, and relatively low cost [35,36], which make it a suitable candidate for energy conversion/storage, high-performance electronics, photocatalysis, sensors, solar cells and supercapacitors [37-41]. In addition, it is applied in environmental remediation [42,43], as biocide and as nanofertilizer in agriculture [44,45].

The synthetic strategy and the careful control of synthesis parameters play a key role in determining the ZnO properties. In addition, environmentally friendly syntheses must be privileged, also on account of the extent of ZnO applications and consequent sizeability

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of the production. Ideally, a green synthesis is performed at room temperature with water solvent and possibly a high yield. In this framework we reviewed the literature, in search of the optimum synthesis conditions. However, when exploring RT syntheses, it appeared that a quite large variety of parameters are included under the RT label, or that additional operations besides RT synthesis are required to achieve pure ZnO.

A common feature to all syntheses is the use of a large excess of base, typically NaOH, with respect to the Zn salt ($Zn(NO_3)_2$, $Zn(CH_3CO_2)_2$), from a minimum of 5 up to 50 times larger. Room temperature synthesis was carried out at 25°C, double jet conditions, controlling the shape and size of ZnO by pH of the solution (pH 9.5 to 10.5). In addition, a surfactant (sodium dodecyl sulfate) was used. Following operations require the precipitate to be washed with distilled water, frozen, and subsequently vacuum dried [46].

A synthesis was carried out at RT (exact value non specified) [47], by keeping the solution sealed and in dark up to 60 days, centrifuged, washed with water and ethanol and then dried under vacuum. XRD indicated the formation of ZnO, though spectra were reported starting from $2\theta > 20°$, whereas signature reflexes of $Zn(OH)_2$ appeared very near to that boundary ($2\theta=20.16°$ and $2\theta=20.89°$) [48]. A synthesis of ZnO nanoparticles as well as micrometric agglomerates was performed at RT by using $Zn(CH_3CO_2)_2$ and a mixture of NaOH and NH_4F in water solution in variable proportions. The reaction was carried out for 10 min, followed by centrifugation, washing with water and ethanol and drying at temperatures between 60°C and 75°C [49]. Sonochemistry was used for 10 min RT synthesis, followed by 2-4h sonication at 40 KHz, filtration, washing with methanol and drying also at RT [50]. In this case, the sonication procedure could be crucial, not only because of the ultrasound waves sent to the sample, but also for the temperature of the bath which tends to increase during the sonication, if not externally controlled. Syntheses at different temperatures by 10°C stepwise increase between 0°C and 80°C were carried out from $Zn(CH_3CO_2)_2$ and NaOH water solutions, followed by centrifugation and washing with water. In this case the drying was achieved by lyophilization [51]. In all cases ZnO is reported as sole product, though XRD patterns start off at $2\theta=0°$, and significant $Zn(OH)_2$ contributions are excluded. In a relatively quick synthetic procedure, ZnO was achieved at RT by precipitation, 30min stirring and 1h ageing. However, drying followed at 60°C, though the length of the latter is not mentioned [52].

A synthesis at RT is reported by Kumar et al. [53] where NH_4OH is added dropwise to a water solution of $Zn(NO_3)_2$ of unspecified concentration under controlled, though not disclosed, pH and ensuing 48h RT drying.

All-in-all, ZnO is either not fully achieved by carrying out operations solely at room temperature, or insufficient details are reported, or, simply, it is not always clear which the room temperature was during the synthetic procedure.

In the current paper, we explore the effects of "room temperature" on the achievement of ZnO and on its structure by carrying out syntheses in aqueous and controlling reaction and drying temperatures in steps of 10°C. The minimum temperature for synthesizing pure ZnO nanoparticles is 40°C, for both phases (reaction and drying), whereas at 30°C, only $Zn(OH)_2$ is achieved. At higher synthesis temperatures ZnO is also obtained, though of larger average size and slightly different volume density and cell parameters. The band gap of ZnO is consistent with the nanoparticle nature of the synthesized samples.

2. Materials and Methods

All chemicals were of reagent grade and used without any further purification. $Zn(NO_3)_2$, and NaOH were purchased from Sigma-Aldrich. All solutions were prepared with deionized water.

The syntheses were carried out according to the following reaction:

$$Zn(NO_3)_2 + 2NaOH \xrightarrow{T_P} Zn(OH)_{2(s)}\,,\; ZnO_{(s)} + 2NaNO_{3(aq)} \xrightarrow{T_D} ZnO_{(s)} + H_2O + 2NaNO_{3(aq)}$$

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where T_P is the temperature of the precipitation reaction and T_D is the drying temperature. More in detail, a 0.1 M $Zn(NO_3)_2$ solution was first prepared in deionized water and stirred for a few minutes until completely dissolved. Then, an equal volume of a 0.1 M NaOH solution was added dropwise to the solution normalized in oil bath at the selected temperature and stirred 24h.

In first instance, in the selection of the synthesis parameters, the ratio between $Zn(NO_3)_2$ and NaOH was kept at 1:1, i.e. in excess of Zn^{2+}. This implies an initial pH of 6, that corresponds to a minimum of ZnO solubility in water (at 25°C) [54], to ensure that formed ZnO does not redissolve. In a typical synthesis, the reaction is carried out at a given temperature (T_P), the slurry digested for two hours, centrifuged (3500 rpm for 10 min), washed with distilled water multiple times and then dried at the chosen temperature (T_D) in an oven for 72 h. A white powder was, then, achieved, which was further characterized. The summary of the syntheses conditions is reported in Table 1.

Table 1. Samples Preparation Conditions.

Sample	Reaction Temperature	Drying Temperature
P30D30	30°C	30°C
P30D40	30°C	40°C
P40D40	40°C	40°C
P50D30	50°C	30°C
P50D50	50°C	50°C
P60D60	60°C	60°C

X-ray diffraction (XRD) patterns of the synthesized samples were collected with an X'pert pro X-ray diffractometer by Philips, using CuK-Alpha radiation. They were, then, analyzed by a Rietveld procedure with the GSAS-II suite of programs [55]. Scanning Electron micrographs (SEMs) were collected with a Zeiss Auriga 405, Field Emission-Scanning Electron Microscope instrument, mounting a Gemini column and operating at 7 kV.

Optical measurements in the ultraviolet (UV), visible (Vis), and near infrared (NIR) spectral regions were obtained by a diffuse reflectance setup from Avantes BV (The Netherlands). The latter comprises a combined deuterium-halogen radiation source (AvaLight-DH-S-BAL) connected via an optical fiber to a 30 mm-diameter Spectralon® coated integrating sphere (AvaSphere-30-REFL used to illuminate the samples (sampling port diameter 6 mm) and collect the radiation diffusely reflected from all angles. . The ZnO powders were placed in the well of a sample holder with a depth such as to be able to consider the reflectance spectra as those of an infinitely thick sample (R_∞). The integrating sphere was connected through another optical fiber to a spectrometer (AvaSpec-2048x14-USB2). This configuration allows applications in the 248–1050 nm range with a 2.4 nm spectral resolution. A laptop is used for spectrometer control and data recording, whereas factory calibrated Spectralon® (Labsphere, USA), is used as reflectance reference. Each reflectance spectrum was obtained by averaging 5 acquisitions lasting 5 seconds each.

3. Results and Discussion

The solvo-synthesis of ZnO can be depicted as a two-stages process, i.e. precipitation and drying. The achievement of the ZnO, rather than $Zn(OH)_2$ or a combination of the two moieties, strictly depends on the operational modalities of two stages.

In the present paper we opted for determining the best match in terms of temperature of each of the two steps, aiming at finding the lowest possible ones, which would

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guarantee no detectable presence of $Zn(OH)_2$. The verification of the composition was primarily carried out by XRD. Additional information on the fine structure of ZnO were determined by Rietveld refinement. A first synthesis was carried at $T_P=T_D=30°C$, hence the closest, in our experimental setup, to the classical definition of RT=25°C. In this setup we obtained nearly 100% $Zn(OH)_2$ samples (Figure 1). We, then, increased the drying temperature by 10°C to achieve the sample P30D40 and, subsequently, also the reaction temperature by 10°C (sample P40D40). The former setup still affords a mixture of ZnO and $Zn(OH)_2$, whereas the XRD of the latter indicates the solely presence of ZnO. We also verified that a temperature of 40°C was strictly necessary to achieve ZnO, by varying the reaction temperature to 50°C and using either 30°C or 40°C for the drying procedure. Once more, the former yields a mixture of ZnO and $Zn(OH)_2$ whereas the latter is pure ZnO. Finally, we performed a synthesis at $T_P=T_D=60°C$ obtaining pure ZnO. Therefore, in general, 40°C is the threshold temperaturenecessary both for the rection and for drying in order to achieve ZnO.

Since RT ZnO syntheses reported in literature are typically carried out in basic conditions, with $Zn(NO_3)_2$ and NaOH ratio 1:5 to 1:50 [51-58] and pH≥12, we verified whether basic conditions would allow lower temperature conditions and carried out a synthesis using a $Zn(NO_3)_2$:NaOH ratio of 1:10, at Tp=Td=30°C. Also in this case we achieved $Zn(OH)_2$ (XRD not shown).

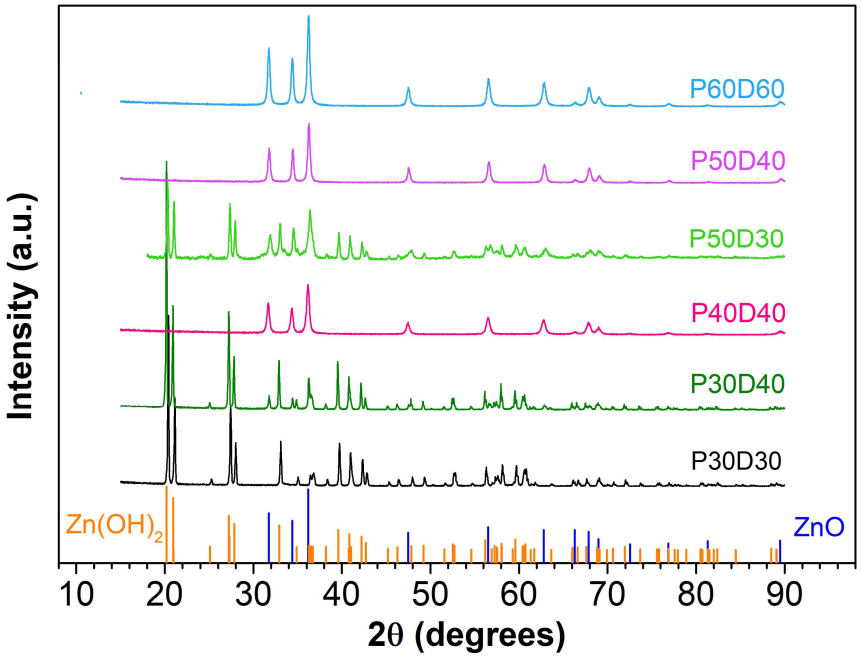

Figure 1. XRD patterns of the synthesized samples.

The powder X-Ray diffraction spectra of all the samples P30D30, P30D40, P40D40, P50D30, P50D40 and P60D60, were first visually compared (Figure 1) and then analyzed with Rietveld refinement using the GSAS-II software [55]. P40D40, P50D40 and P60D60 proved to be composed of pure ZnO, and the difference of the structural parameters was investigated, whereas P30D30, P30D40, and P50D30, on the contrary, turned out to contain both the target product (ZnO) and the precursor $Zn(OH)_2$. For this reason, the relative composition of the two solid phases in the mixture was assessed besides the structural parameters. The preliminary qualitative comparison of the spectra pointed out that in P60D60, P50D40, P40D40- the first three patterns reported in Figure 1 - the peak positions are similar, the only notable difference being their intensity that is highest for P60D60 and comparable in the other two systems. A common crystal structure can

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therefore be envisaged for them. A more accurate analysis, though, (see Figure 2), shows that the most intense peaks from P60D60 fall almost in the middle between P40D40 peaks (lower angle) and P50D50 ones (higher angle); the latter two sets of peaks are shifted by 0.1 degrees, on average.

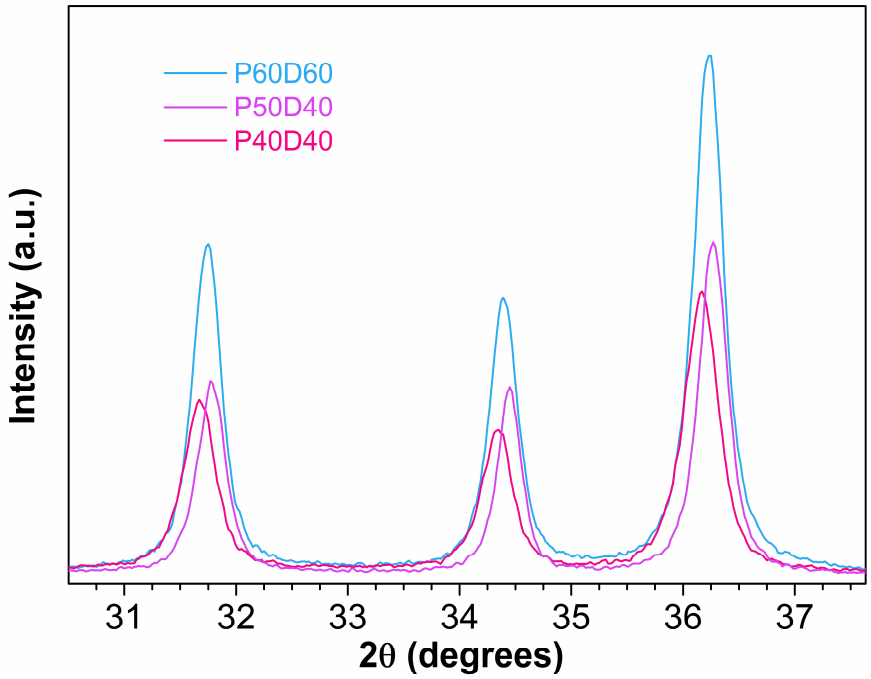

Figure 2. Details of pure zinc oxide samples XRD patterns

This issue suggests that a slight change of some crystal parameter(s) occurs among the three structures. Regarding P30D40, P30D30, and P50D30, the patterns are characterized by a large number of new peaks that show up in all angle ranges, especially the very intense ones before 30 degrees, a portion of the spectrum where no peaks are found in P60D60, P50D40 and P40D40. The crystal structures of the mineral zincite (100% ZnO, space group P63mc) [56] and of Wulfingite (pure zinc hydroxide, P212121) [48] were then employed in the fitting procedure. Both single-crystal phase data were downloaded from the American Mineralogist Crystal Structure Database [57] as Crystallographic Information Files (CIF). The simulated powder pattern for each sample was obtained, for CuKα wavelength (1.54 Å), modelling the peak shapes with a convolution of modified asymmetric pseudo-Voigt functions [58]. The background was modelled with a 3-term Chebyshev polynomial of the first kind. P60D60 profile was successfully fitted on 3100 observations, reaching the weighted-profile R factor wR = 11.76%, R=8.20%, χ^2 = 5420.14 at convergence. The same approach was adopted for the other systems, obtaining wR = 14.96%, R=10.83%, χ^2 = 6382.69 for P50D40; wR= 14.16%, R= 9.79%, χ^2 = 5254.82 for P40D40; wR= 24.82%, R= 17.94%, χ^2 = 3188.23 for P30D40, wR= 17.36 %, R= 13.09 %, χ^2 = 15145.9 for P30D30; wR= %, R= 17.36%, χ^2 = 15153.9 for CM9 and wR= 24.82%, R= 17.94% and χ^2 = 3188.23 for P50D30. The ratio between oxide and hydroxide phase fractions in the mixtures was fitted as well, obtaining the following ZnO:$Zn(OH)_2$ ratios: 22:78, 0.05:99.5, 85:15 and 69:31 for P30D40, P30D30 and P50D30 respectively. The fitting plots are reported in the Supplementary Information figures SI1 through SI6. The sample P30D30 will be from now on considered as pure hydroxide for simplicity. The fitting procedure also returns the optimized structural parameters for the cell(s) and the atom positions; additional fitted parameters were the domain size and microstrain of the crystallites, as well as the sample position and the instrumental broadening parameters U, V, W. The

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most important parameters are reported in the tables below (Table 2 for pure ZnO, Table 3 for the mixtures).

Table 2. Pure ZnO systems. Fitted cell parameters, domain sizes and fractional coordinates

Sample	a (Å)	b (Å)	c (Å)	Volume (Å^3)	Density (gcm^{-3})	Dom. Size (μm)
P40D40	3.24009	3.24009	5.20890	47.358	5.707	0.0469
P50D40	3.31864	3.31864	5.14557	49.078	5.507	0.0848
P60D60	3.27670	3.27670	5.20890	48.434	5.580	0.0791
Fractional coordinates	**X (Zn)**	**Y (Zn)**	**Z (Zn)**	**X (O)**	**Y (O)**	**Z (O)**
P40D40	0.33333	0.66667	-0.04651	0.33333	0.66667	0.34516
P50D40	0.33333	0.66667	-0.02259	0.33333	0.66667	0.36759
P60D60	0.33333	0.66667	-0.02279	0.33333	0.66667	0.36779

Table 3. Mixed ZnO/Zn(OH)$_2$ systems. Fitted cell parameters, domain sizes and fractional coordinates

Sample/Phase	a (Å)	b (Å)	c (Å)	Volume (Å^3)	Density (gcm^{-3})	Dom. Size (μm)	Fraction		
P30D40									
ZnO	3.25866	3.25866	5.20629	47.878	5.645	0.0961	22.46%		
Zn(OH)$_2$	4.90609	5.14418	8.47285	213.836	3.087	0.2682	77.54%		
Fractional coordinates	**X(Zn)**	**Y (Zn)**	**Z (Zn)**	**X(O1)**	**Y (O1)**	**Z (O1)**	**X(O2)**	**Y (O2)**	**Z (O2)**
ZnO	0.33333	0.66667	-0.01969	0.33333	0.66667	0.36469			
Zn(OH)$_2$	0.07118	0.65017	0.62232	0.12575	0.12791	0.07742	0.18748	0.31445	0.72972
Sample/Phase	**a (Å)**	**b (Å)**	**c (Å)**	**Volume (Å^3)**	**Density (gcm^{-3})**	**Dom. Size (μm)**	**Fraction**		
P30D30									
Zn(OH)$_2$	4.66647	5.45967	8.36003	212.992	3.100	0.2865	≈100%		
Fractional coordinates	**X(Zn)**	**Y (Zn)**	**Z (Zn)**	**X(O1)**	**Y (O1)**	**Z (O1)**	**X(O2)**	**Y (O2)**	**Z (O2)**
Zn(OH)$_2$	0.06814	0.65039	0.62453	0.11409	0.13244	0.08367	0.19477	0.31458	0.73196
Sample/Phase	**a (Å)**	**b (Å)**	**c (Å)**	**Volume (Å^3)**	**Density (gcm^{-3})**	**Dom. Size (μm)**	**Fraction**		
P50D30									
ZnO	3.24544	3.24544	5.20182	47.450	5.696	0.0392	68.98%		
Zn(OH)$_2$	4.89683	5.13368	8.45536	212.557	3.106	10.0	31.02%		
Fractional coordinates	**X(Zn)**	**Y (Zn)**	**Z (Zn)**	**X(O1)**	**Y (O1)**	**Z (O1)**	**X(O2)**	**Y (O2)**	**Z (O2)**
ZnO	0.33333	0.66667	-0.02452	0.33333	0.66667	0.36952			
Zn(OH)$_2$	0.06752	0.64093	0.62973	0.13339	0.11871	0.09189	0.15829	0.35522	0.71823

An interesting feature pointed out during the refinement was the difference in the cell parameters of the three pure zinc oxide samples. The cell parameters refinement confirms that P60D60 has an intermediate behavior with respect to P50D40 and P40D40. The cell dimensions and the resulting volume (and density) fall in the middle of the range, in compliance with the peak positions already discussed above. The density order P40D40> P60D60>P50D40 is nicely anticorrelated with the position of the peaks, i. e.

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P40D40, the densest structure, having structural correlations that occur at smaller distance on average, gives origin to diffraction peaks that fall at larger angles (according to the scattering vector and Bragg's law definitions $Q=4\pi\sin\theta/\lambda$ and $d=2\pi/Q$ [59,60])while the distances between the atoms contained in the least dense sample (P50D40) are typically larger and the resulting peaks fall at smaller angle. Interestingly, the cell dimensions are proportional to the average (fitted) dimension of the crystallites, signaling that smaller nanoparticles (P40D40) occupy the smallest volume, i.e. they are more efficiently packed. When compared with the single-crystal cell dimensions (a=3.24950 c=5.2069), or with some recently reported ZnO nanosheets (a= 3.245 c=5.198, [61], the first two nanoparticle samples appear to be significantly less dense, while P40D40 values are much closer. The calculated density values confirm this trend and satisfactorily comply with the experimental density value of 5.61 g cm^{-3} [62]. The modulation of the structural features observed demonstrates that our synthesis protocol, by a simple tuning of the temperature., is capable of leading, easily and successfully, to final products with different properties.

The synthesized samples display different types of morphology, depending on the temperature adopted in the different phases of the synthesis. Examples of the morphology of the samples are reported in Figure 3. The P30D30 sample, mostly composed of $Zn(OH)_2$, has micrometric structure of aggregated foils. In the P30D40 sample the micrometric arrangements become more compact to form blocks and some nanoparticles appear on their surface highlighted in Figure 3b with light orange circles. Once pure ZnO is formed, i.e. when both reaction and drying temperatures are, at least, 40°C, the samples are characterized by the shear presence of nanoparticles. The nanoparticle morphology of ZnO is kept also for higher synthesis temperature, though the average size is slightly larger. In particular, the average size of the P40D40, P50D40 and P60D60 are 53±10 nm, 65±12 nm and 69±11 nm, respectively, thus in agreement with the crystallite size detected by XRD, within the experimental error. In addition, there is a good agreement between estimated crystallite size and the samples morphology, for mixed $Zn(OH)_2$/ZnO samples with larger average size associated to $Zn(OH)_2$ as compared to ZnO. XRD allows a separate assessment of the average size of each phase. Though this is not possible by SEM imagining, since the morphology cannot quite distinguish the crystallographic phase, it can be hypothesized that the small nanoparticles on the surface of the blocks in the P30D40 sample are actually ZnO deriving from the $Zn(OH)_2$ dehydration.

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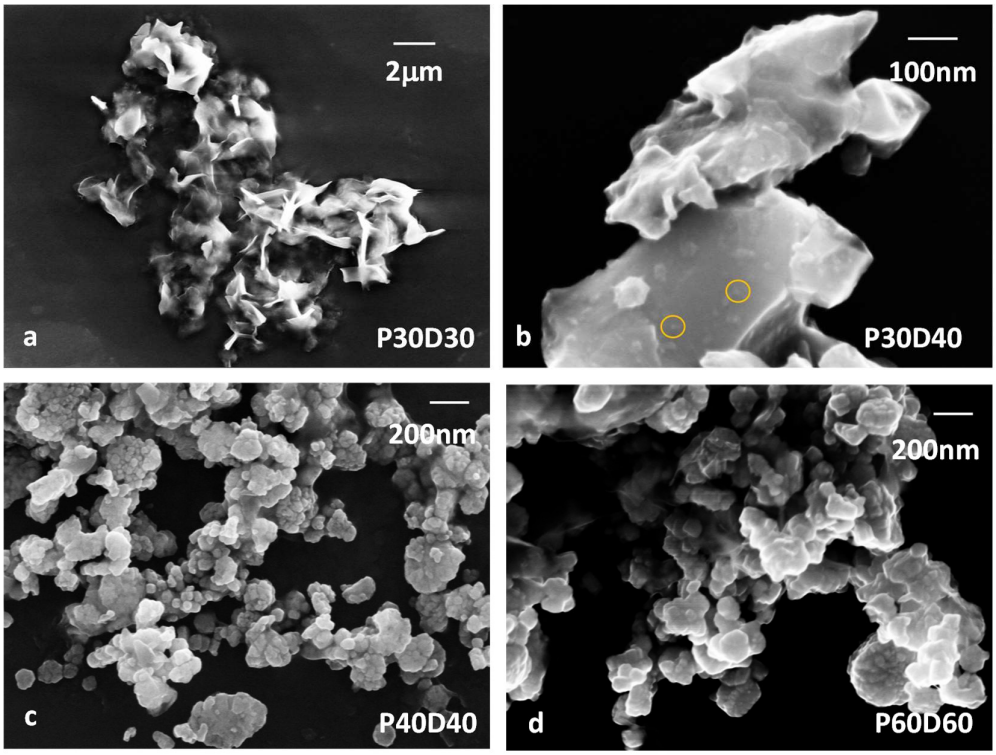

Figure 3. Selected SEM images of the synthesized samples: a) P30D30, b) P30D40, c) P40D40, d) P60D60.

The band gap of the ZnO nanoparticles samples was estimated by diffuse reflectance R_∞ spectra, where R_∞ is the reflectance of an infinitely thick layer of sample, converted into absorption spectra by using the Kubelka-Munk function [63,64]:

$$\frac{K}{S} \equiv \frac{(1-R_\infty)^2}{2R_\infty}$$

where *K* and *S* are the Kubelka–Munk absorption and scattering coefficient, respectively... The K absorption coefficient is related to the intrinsic absorption coefficient of the particles α by $\alpha = K/2$, in case of diffuse light distribution as in our case [65]. The steady preparation of ZnO powder sample for optical measurements also allowed us to consider *S* constant from sample to sample, then the ratio $K/S \approx \alpha$. In order to estimate the band gap from the absorption spectra we can, then, apply the Tauc relation [66]:

$$\alpha h\nu = C1(h\nu - E_g)^n$$

Where n=1/2 for indirect gap and n=2 for direct gaps, such as the case of ZnO, and C1 is a constant.

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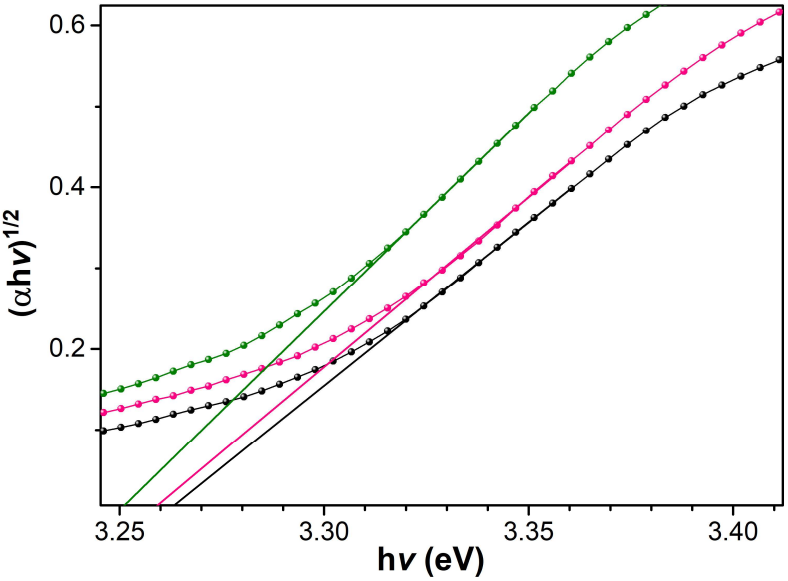

Figure 4. Tauc plots for the determination of optical band gap E_g (lines+dots) and associated extrapolations of the linear regions (solid lines). Green corresponds to the sample P40D40, red to P50D40 and black to P60D60.

The ZnO band gap E_g including the quantum confinement as a function of the average particle size is obtained from the effective mass model given by [67,68]:

$$E_g \cong E_g^{bulk} + \frac{h^2}{8e\mu r^2} - \frac{1.8e}{4\pi\varepsilon_r\varepsilon_0 r} - \frac{0.124e^3\mu}{(2h\varepsilon_r\varepsilon_0)^2}$$

In this equation all terms are in eV, E_g^{bulk} is the bulk ZnO band gap (3.35 eV), h is the Planck constant, r is the particle radius, e is the charge of the electron, μ is the reduces mass of electron and holes $\mu = \frac{m_e^* m_h^*}{m_e^* + m_h^*}$, where m_e^* and m_h^* are the effective mass of the electrons and holes in ZnO, respectively, $m_e^* = 0.19m_e$ and $m_h^* = 0.8m_e$, where m_e is the free electron mass [69]; ε_r (3.7) is the relative permittivity, ε_0 is the permittivity of free space.

The Eg values of 3.25(0), 3.25(8) and 3.26(2) eV (Table 4) injected in the previous equation all yields nanoparticles sizes (2r) of about 15 nm, providing an estimation of the smaller size in the synthesized ZnO nanoparticles.

Table 4. Band gap of the ZnO samples.

Sample	Band Gap (eV)
P40D40	3.25(0)
P50D40	3.25(8)
P60D60	3.26(2)

Compared to a band gap of 3.35 eV in bulk ZnO [70], P40D40, P50D40, P60D60 exhibit a red shift by ~0.1 eV. ZnO nanoparticles, in general, may undergo both a blue and a red shift, many factors concurring to the actual band gap value. As shown by Eq. 1, below 14 nm diameter threshold, the size effect is dominant and a blue shift is observed [71,72]. However, also the shape plays a role and both red and blue shift, depending on the particles morphology, as determined by the employment of different solvents during the synthesis [73]. In RT synthesis followed by lyophilization, a red shift by ~0.1 eV has been

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observed between synthesis at 20°C and at 50°C and it has been associated to a slight size increase of the nanoparticles [51]. However a simultaneous shape change was also observed from elliptical to conical which may also contribute to the red shift. P40D40, P50D40, P60D60 have similar morphologies and the comparable band gap values would indicate similar average sizes. Comparison with XRD results, which give domain sizes ranging from 46.9 to 84.8 nm, suggests a shape anisotropy for the P40D40, P50D40 and P60D60 nanoparticles, which can be also observed from SEM images (Figure 3 c and d). It must be added that the average particles size in band gap corresponds to the pathway for an electronic transition through a gap, which can be equivalent for anisotropic samples, with similar minimum size pathway.

4. Conclusions

Room temperature synthesis of ZnO nanoparticles in aqueous solution has been achieved. The synthesis has been carried out by controlling reaction and drying temperature, without the aid of any surfactant, pumping or freezing. We found out that the minimum temperature for achieving ZnO is 40°C for both synthetic phases. Lowering any of the two temperatures results in the achievement of $Zn(OH)_2$ or a mixture $Zn(OH)_2$/ZnO. Beyond the threshold value of 40°C, ZnO nanoparticles are still obtained, though with larger average size and different density. The morphology is similar for all ZnO nanoparticles as well as the optical band gap. The morphology of lower temperature samples indicates the presence of aggregated foils, which merge to form blocks, from which ZnO nanoparticles eventually detach. The results obtained from SEM experiments comply quite well with X-Ray diffraction experiments and optical analysis of the band gap, where it was found that the scattering patterns observed for the samples synthesized at temperatures larger than 40°C show a shape anisotropy and an evident shift towards smaller angles, thus indicating systems of larger average dimensions and crystallites size.

Supplementary Materials: Figures S1 through SI6: XRD patterns of the samples P30D30, P30D40, P40D40, P50D30, P50D40, P60D60 and associated Rietveld fits.

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