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Structural study and phase transition investigation in a simple synthesis of porous architected-ZnO nanopowder

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A B S T R A C T

In this work, zinc oxide powder with a rectangular-shaped porous architecture, made of numerous spherical nanometric particles, was obtained. A simple precipitation/decomposition procedure was used comprising a zinc oxalate intermediate, obtained from zinc sulfate and oxalic acid without any additives. Detailed studies on zinc oxalate dehydration, decomposition and zinc oxide formation, were carried out using in-situ temperature X-ray diffraction and thermogravimetric analysis. During the investigation, the temperature dependence of particle sizes, lattice parameters and crystal structures of $\text{ZnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, ZnC_2O_4 and ZnO nanopowders were analyzed from room temperature to 450 °C. Structural transitions were also discussed. The structure and morphology of the as-prepared ZnO nanopowder were investigated by electron microscopy and compared to the crystalline rectangular shape of $\text{ZnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$. The calcination temperature, counter ion and precipitate agent were found to be related to the product's shape and diameter. Spherical ZnO nanoparticles with diameters of less than 20 nm and a maximum specific surface of 53 m²/g were obtained using this method.

Keywords:

Oxides

Nanostructures

Chemical synthesis

Crystal structure

Phase equilibria

1. Introduction

Zinc oxide (ZnO) has been attracting a lot of attention for its various applications, such as semi-conductor devices, photo catalysts, pigments in paints and photovoltaic uses [1–6]. The well-known properties, such as the wide direct band-gap (3.3 eV), large exciton binding energy (60 meV), low cost, environmental friendly and abundance, make it a very interesting material. For different applications, ZnO can be used in various forms and morphologies [7–13]. Syntheses of powdered form ZnO using wet chemistry methods have already been widely reported [14–20]. There are a lot of parameters during synthesis that can affect the structure and microstructure of ZnO which are essential for their performance [17–19]. Thermal decomposition of zinc oxalate has been reported to produce porous and relatively high specific

surface ZnO [6] which is especially interesting for gas sensing, photovoltaic or photocatalysis applications [21,22,12]. In the particular case of dye sensitized solar cells (DSSC), ZnO was reported as a good alternative of the conventional TiO_2 semiconductor material for the first time in 1994 [23]. Since then, a lot of works focused on the development of new DSSC nanostructured photo-anodes made of ZnO porous nanostructures with various morphologies (nanowire, nanosheet, branched-nanostructure of multi-layers material, nanowire-nanoparticle composite, ...) have been reported [24,9,25–27] reaching an overall DSSC efficiency for more than 7% [28].

In the present work, the precipitation of ZnC_2O_4 -based precursor in hydro-alcoholic medium was carried out first, followed by in-situ high temperature X-ray diffraction analysis of the precursor from 50 to 450 °C. Detailed structural and

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micro-structural studies were performed for each of the crystalline structures obtained. Finally, ZnO nanopowder with porous architecture was prepared through the obtention and thermal decomposition of zinc oxalate di-hydrate and anhydrous intermediates.

2. Experimental

2.1. Material Preparation

All the chemicals were of analytical purity grade and used as received. The raw materials used were $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ and $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ as sources of oxalate and zinc respectively. A solution of 0.02 mol of oxalic acid in a mixture of 192 ml of ethanol and 64 ml of water, was added dropwise into 128 ml of an equimolar solution of zinc salt in distilled water. After stirring for 1 h at room temperature, a white precipitate was obtained and separated by centrifugation and washed several times with distilled water by centrifugation again. This precipitate was dried at 80 °C for several hours to attain the $\text{ZnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ powder precursor. A detailed study of the thermal behavior of $\text{ZnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ was performed up to 450 °C, which is a temperature compromise in DSSC application between obtaining good electronic contacts and maintaining high porosity while respecting the conducting glass support stability [29]. Finally, the characteristics of the zinc oxide obtained were investigated after cooling down to room temperature.

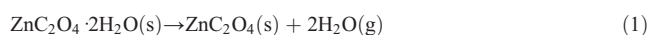
2.2. Material Characterization

The structural and microstructural studies of the precursors and products were carried out using the following equipments and techniques. One point Brunauer–Emmett–Teller (BET) measurement was obtained with N_2 as absorption gas at 77 K by using a Micromeritics FlowSorb II 2300 apparatus. Microstructural images were produced from scanning electron microscopy (SEM) using a Field Emission Gun SEM JEOL JEM 6700F. Conventional and temperature dependent powder X-ray diffraction (XRD) analyses were performed by using

Bruker D4 Endeavor and D8 Advance diffractometers respectively, both equipped with a 1D LynxEye detector ($\text{Cu K}\alpha$). For temperature dependent XRD, the sample was heated in an Anton Paar HTK 1200 N heating chamber with a 30 °C/min heating rate. XRD patterns were recorded every 25 °C from room temperature to 450°C with a 20 min counting time. Rietveld refinements of the XRD patterns were performed using the FullProf/Win PlotR software package, in which the background was estimated by linear interpolation, and the peak shape was modeled by a pseudo-Voigt function. The observed profile parameters extracted from the Rietveld analysis (FWHM^{obs}), coupled with the instrumental broadening ($\text{FWHM}^{\text{inst}}$) determined from a standard reference material ($\alpha\text{-Al}_2\text{O}_3$), were used to calculate the mean crystallite apparent size (ϵ), by applying the Williamson–Hall plot ($(\text{FWHM}^{\text{obs}} - \text{FWHM}^{\text{inst}})\cos\theta = f(\sin\theta)$) [30]. Thermogravimetric analysis (TGA) was performed with a SETARAM DT-TGA 92B thermo-balance under air atmosphere with a heating rate of 3 °C/min.

3. Results and Discussion

Fig. 1 shows the successive characteristic evolution of the XRD patterns (2θ from 17.5° to 40°) recorded upon heating, from 50 to 450 °C for every increment of 25 °C, during the decomposition of the oxalate precursor. The corresponding TGA plot of this precursor is shown in Fig. 2. Both TGA and XRD analyses show that the zinc oxalate dihydrate precursor ($\text{ZnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$) decomposes first to anhydrous zinc oxalate (ZnC_2O_4) at ~125 °C and then to zinc oxide (ZnO) at ~355 °C according to the following reactions:



The two experimental TGA weight losses of 18.5% and 37.8% correspond closely to the calculated values (19.0% and 38.0%) based on reactions (1) and (2).

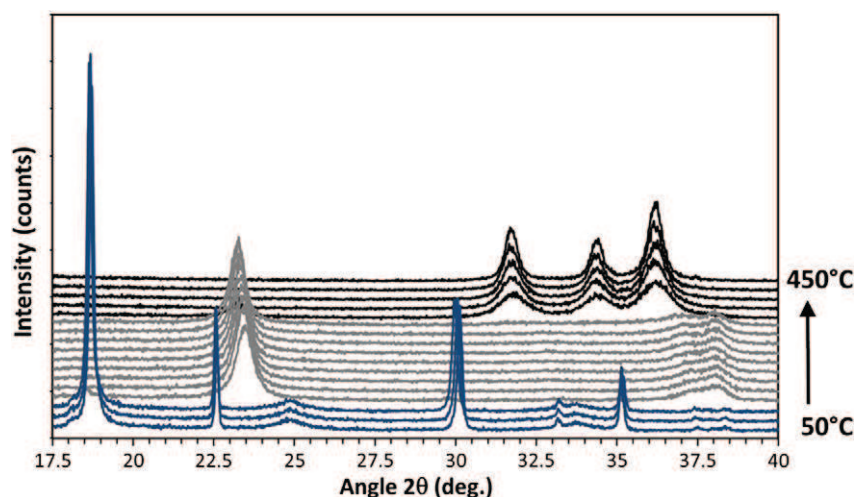


Fig. 1 – Temperature XRD patterns in the 50 to 450 °C temperature range for zinc oxalate precursor.

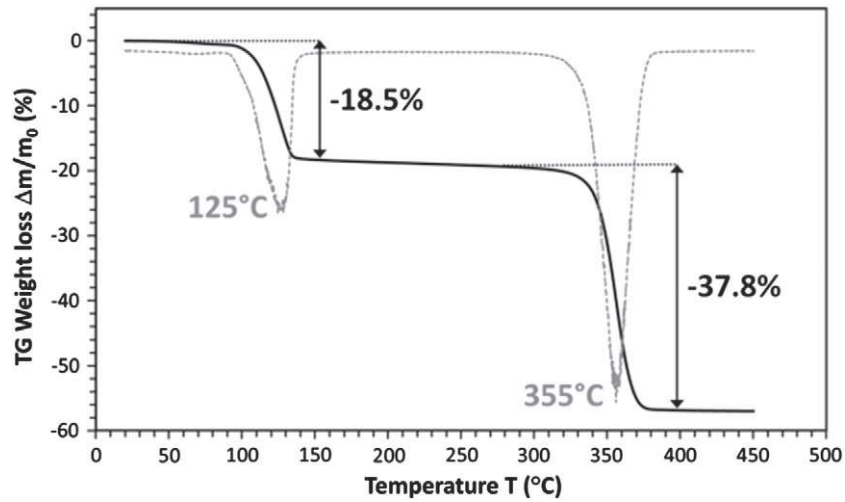


Fig. 2 – TGA/DTG curves in the 50 to 450 °C temperature range for zinc oxalate precursor.

3.1. Zinc Oxalate Dihydrate ($\text{ZnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$)

At room temperature, the oxalate precursor which was directly obtained after precipitation corresponds to the pure metastable orthorhombic β form of the zinc oxalate dihydrate ($\beta\text{-ZnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$). As no doublet peak located at $2\theta / \lambda_{\text{CuK}\alpha} \sim 18.74^\circ$ is clearly visible, there is no particular reason to index the XRD pattern according to the monoclinic α form (humboldtine). This result is in good agreement with previous reports of metal oxalate dihydrate synthesized in a hydro-alcoholic solution [31,32]. The refined cell parameters determined for this zinc oxalate dihydrate phase in orthorhombic $Cccm$ space group are reported in Table 1 (a_0 , b_0 and c_0) at 50, 75 and 100 °C. In this temperature range, the cell parameters are almost constant, the

calculated X-ray density is equal to $\rho = 2.50 \text{ g/cm}^3$ and the mean crystallite size is approximately $\varepsilon \sim 100 \text{ nm}$. In the structure that is represented in a 3D perspective view in Fig. 3a, the zinc cation is six-fold coordinated: four oxygen anions that belong to the oxalate groups form $-\text{C}_2\text{O}_4-\text{Zn}-\text{C}_2\text{O}_4-\text{Zn}-$ chains along the b_0 axis and two apical oxygen anions that belong to the water molecules located along the a_0 axis.

3.2. Zinc Oxalate Anhydrous (ZnC_2O_4)

At 125 °C, the dehydration induces a structure reconfiguration toward anhydrous zinc oxalate ZnC_2O_4 , isostructural with $\beta\text{-MC}_2\text{O}_4$ where $M = \{\text{Fe, Co, Ni, Zn, Cu, ...}\}$ [33]. The refined cell parameters in monoclinic $P2_1/n$ space group (a_m , b_m , c_m and β)

Table 1 – Refined unit cell parameters, X-ray densities and mean crystallite apparent sizes of $\text{ZnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, ZnC_2O_4 and ZnO materials in the 50 to 450 °C temperature range.

T (°C)	Compound	Space group	a (Å)	b (Å)	c (Å)	β (°)	V (Å ³)	ρ (g/cm ³)	ε (nm)
50	$\text{ZnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$	C ccm	11.863 (3)	5.395(1)	15.718(5)		1006.5 (8)	2.500 (2)	120
75	$\text{ZnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$	C ccm	11.875 (2)	5.3910 (7)	15.720 (4)		1006.8 (6)	2.499 (2)	115
100	$\text{ZnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$	C ccm	11.910 (2)	5.3886 (8)	15.734 (4)		1009.9 (6)	2.492 (2)	110
125	ZnC_2O_4	P 2 ₁ /n	6.042 (5)	5.24 (1)	5.253 (4)	116.0 (1)	149.5 (7)	3.41 (2)	15
150	ZnC_2O_4	P 2 ₁ /n	6.025 (9)	5.28 (1)	5.255 (4)	115.60 (7)	151.2 (6)	3.37 (1)	17
175	ZnC_2O_4	P 2 ₁ /n	6.013 (5)	5.297 (6)	5.246 (3)	115.20 (4)	151.3 (4)	3.37 (1)	17
200	ZnC_2O_4	P 2 ₁ /n	6.014 (6)	5.302 (7)	5.245 (3)	115.13 (4)	151.4 (4)	3.36 (1)	16
225	ZnC_2O_4	P 2 ₁ /n	6.016 (6)	5.294 (7)	5.241 (3)	115.21 (4)	150.9 (4)	3.37 (1)	17
250	ZnC_2O_4	P 2 ₁ /n	6.024 (6)	5.319 (7)	5.245 (3)	115.18 (4)	151.9 (4)	3.35 (1)	17
275	ZnC_2O_4	P 2 ₁ /n	6.030 (6)	5.313 (7)	5.237 (3)	115.23 (5)	151.2 (4)	3.37 (1)	17
300	ZnC_2O_4	P 2 ₁ /n	6.040 (6)	5.329 (6)	5.242 (3)	115.19 (4)	152.2 (4)	3.35 (1)	18
325	ZnC_2O_4	P 2 ₁ /n	6.051 (6)	5.337 (8)	5.249 (3)	115.13 (4)	153.3 (5)	3.32 (1)	18
350	ZnO	P 6 ₃ /mmc	3.253 (9)		5.22 (1)		47.8 (4)	5.65 (5)	10
375	ZnO	P 6 ₃ /mmc	3.257 (5)		5.223 (7)		48.0 (2)	5.63 (3)	12
400	ZnO	P 6 ₃ /mmc	3.259 (4)		5.217 (6)		47.9 (2)	5.64 (2)	15
425	ZnO	P 6 ₃ /mmc	3.259 (4)		5.222 (6)		48.0 (2)	5.63 (2)	19
450	ZnO	P 6 ₃ /mmc	3.260 (4)		5.223 (6)		48.1 (2)	5.62 (2)	20
50	ZnO	P 6 ₃ /mmc	3.250 (3)		5.209 (5)		47.6 (1)	5.67 (2)	20
50	ZnO	P 6 ₃ /mmc	3.250 (3)		5.209 (5)		47.6 (1)	5.67 (2)	20
450	ZnO	P 6 ₃ /mmc	3.260 (3)		5.222 (4)		48.0 (2)	5.62 (2)	22
50	ZnO	P 6 ₃ /mmc	3.250 (3)		5.209 (4)		47.6 (2)	5.67 (2)	22

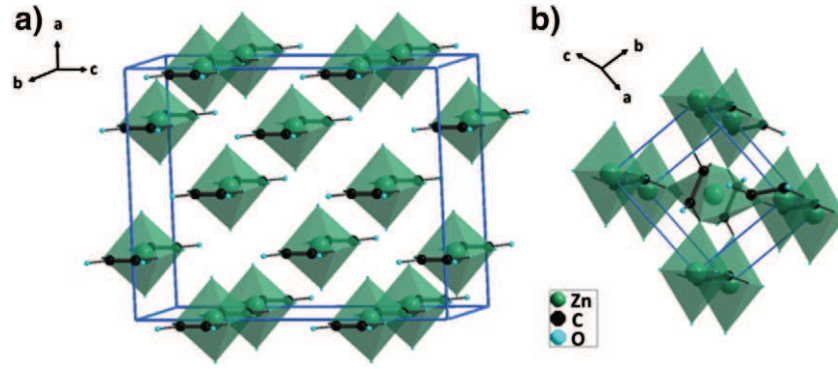


Fig. 3 – Schematic representations in perspective 3D view of the a) $\text{ZnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ and b) ZnC_2O_4 zinc oxalates structures.

are listed in Table 1. In this structure, every zinc atom is surrounded by six oxygen atoms, forming highly distorted octahedra which are connected to one another through corners. These six oxygen atoms all belong to oxalate groups. The first four oxygen anions are located at two similar distances from the central zinc atom ($d(\text{Zn}-\text{O})_1 = 1.98 \text{ \AA}$ and $d(\text{Zn}-\text{O})_{1'} = 2.01 \text{ \AA}$ at $125 \text{ }^\circ\text{C}$). They all form $-\text{C}_2\text{O}_4-\text{Zn}-\text{C}_2\text{O}_4-\text{Zn}-$ chains along the c_m axis (Fig. 3b). These chains with $d(\text{Zn}-\text{Zn}) = c_m = 5.253(4) \text{ \AA}$ in ZnC_2O_4 at $125 \text{ }^\circ\text{C}$, correspond to the chains that already exist in $\text{ZnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, with slightly lower zinc to zinc distances ($d(\text{Zn}-\text{Zn}) = b_o = 5.3886(8) \text{ \AA}$ in $\text{ZnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ at $100 \text{ }^\circ\text{C}$), due to the disappearance of the weak hydrogen bonds. The dehydration simultaneously induces a tilt of the $-\text{C}_2\text{O}_4-\text{Zn}-\text{C}_2\text{O}_4-\text{Zn}-$ chains located at $x = \frac{1}{4}$ around the b_o axis of the $\text{ZnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ structure. This allows one to complete the coordination of the distorted ZnO_6 octahedron in the anhydrous structure, with the two last oxygen anions located at $d(\text{Zn}-\text{O})_2 = 2.36 \text{ \AA}$. These two sets of $d(\text{Zn}-\text{O})$ are confirmed in Raman spectroscopy by characteristics peaks located at 228 and 267 cm^{-1} (Fig. 4), which are attributed to metal-oxygen stretching vibrations and are in good agreement with previous reports [34].

In the 125 to $325 \text{ }^\circ\text{C}$ temperature range, a_m and c_m parameters are quite stable ($+0.16$ and -0.08% respectively), whereas the b_m parameter significantly increases ($+1.79\%$). The calculated X-ray density then decreases from $\rho = 3.41 \text{ g/cm}^3$ to $\rho = 3.32 \text{ g/cm}^3$ in this temperature range. The mean crystallite size is stable at

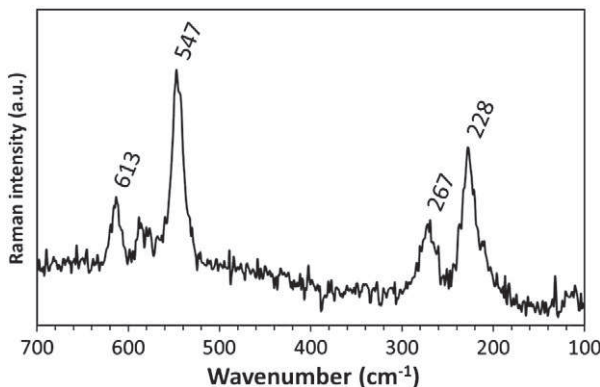


Fig. 4 – Raman spectra of the $100\text{--}700 \text{ cm}^{-1}$ region of ZnC_2O_4 .

$15 < \varepsilon < 20 \text{ nm}$. The anisotropy of the thermal dilatation leads to an increase in the distortion of the ZnO_6 octahedron. The Zn to O bond length ($d(\text{Zn}-\text{O})_2$), which was already large in comparison to the theoretical value ($d(\text{Zn}^{2+}_{\text{VI}}-\text{O})_{\text{th}} = 2.14 \text{ \AA}$ [35]), continues to increase and tends to weaken the Zn-O bond strength. At $T \sim 350 \text{ }^\circ\text{C}$, the structure is unstable and hence the process of structure-reconfiguration consists of the following sequence of consecutive bond breaking: the two longest Zn-O bonds, the four other Zn-O bonds, then the C-C bonds which results to the generation of a free CO_2 molecule. This pattern is in accordance with first principle calculations, performed by Kolezynski et al. [36], of band structure, density of states, electron density topology, bond orders and valences.

3.3. Zinc Oxide (ZnO)

Above $350 \text{ }^\circ\text{C}$, pure zinc oxide with a wurtzite structure is obtained. In this structure, the zinc atoms are in tetrahedral coordination. The refined cell parameters in hexagonal $P6_3/mmc$ space group (a_h and c_h) are listed in Table 1. From $350 \text{ }^\circ\text{C}$ to $400 \text{ }^\circ\text{C}$, as shown in Table 1, the lattice parameters vary rapidly due to the process of structure reconfiguration from the anhydrous oxalate structure to ZnO. Above $400 \text{ }^\circ\text{C}$, a_h and c_h converge to reproducible values obtained for ZnO upon further cooling and heating treatments with $a_h = 3.260(4) \text{ \AA}$ and $c_h = 5.223(6) \text{ \AA}$ at $T = 450 \text{ }^\circ\text{C}$. The calculated thermal expansion coefficients $\alpha_a = 7.7 \cdot 10^{-6} \text{ K}^{-1}$ and $\alpha_c = 6.7 \cdot 10^{-6} \text{ K}^{-1}$ in the RT- $450 \text{ }^\circ\text{C}$ temperature range defined by $\alpha_a = (1/a)(da/dT)$ or $\alpha_c = (1/c)(dc/dT)$ and the ratio, $c_h/a_h = 1.60$, at $450 \text{ }^\circ\text{C}$ are in good accordance with literature values [37]. In the $350\text{--}450 \text{ }^\circ\text{C}$ temperature range, while $350 \text{ }^\circ\text{C}$ is the lowest temperature at which ZnO could be obtained, the mean crystallite size increases from $\varepsilon = 10 \text{ nm}$ to $\varepsilon = 20 \text{ nm}$ with no crystallite shape anisotropy as previously reported by Audebrand et al. [38].

At room temperature, the lattice parameters of the so-obtained ZnO material are $a_h = 3.2503(2) \text{ \AA}$ and $c_h = 5.2091(3) \text{ \AA}$ with a calculated X-ray density of $\rho = 5.67 \text{ g/cm}^3$ (Table 1). The corresponding SEM images with those of the $\text{ZnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ precursor are presented in Fig. 5. The ZnO porous architecture, confined in a sub-micronic rectangular shape (Fig. 5b), consists of a large number of homogeneous nanometric spherical zinc oxide particles (Fig. 5c). Its specific surface, $S_{\text{BET}} = 34 \text{ m}^2/\text{g}$, corresponds to an estimated particle size of $D_{\text{BET}} = 31 \text{ nm}$ defined by $D_{\text{BET}} = 6 \times 10^4 / \rho \times S_{\text{BET}}$ with $\rho = 5.67 \text{ g/cm}^3$ (Table 1). This particle size is

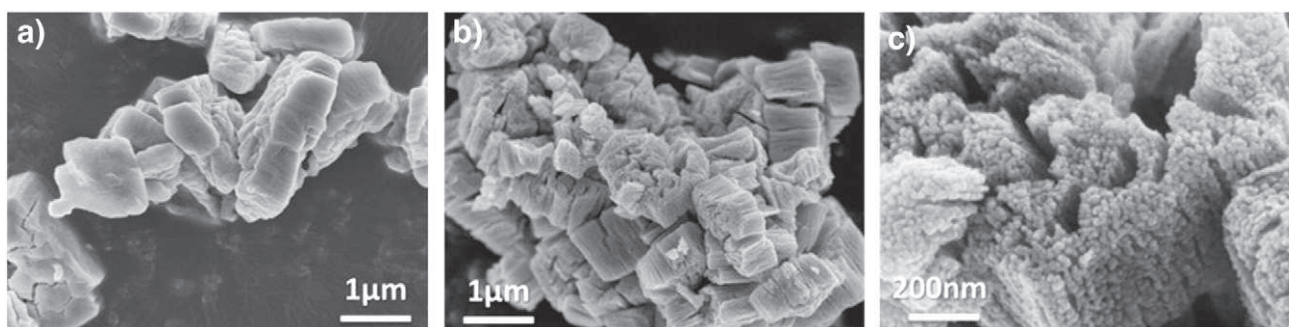


Fig. 5 – SEM micrographs of a) $\text{ZnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, b) ZnC_2O_4 and c) ZnO .

consistent with XRD and SEM measurements with $D_{\text{XRD}} = 27$ nm ($D_{\text{XRD}} = 4/3 \varepsilon$ because the particles are spherical) and $D_{\text{SEM}} = 20\text{--}40$ nm respectively.

The particle size of the ZnO nanopowder in this porous architecture is temperature dependent due to the merging of the smaller particles into larger ones through solid state diffusion [39]. For ZnO prepared by the same process but decomposed only at 350 °C, the particle size is approximately 50% smaller than that of 450 °C with $D_{\text{BET}} = 20$ nm ($S_{\text{BET}} = 53$ m²/g) and $D_{\text{XRD}} = 13$ nm, whereas at 500 °C, the particle size increases up to $D_{\text{XRD}} = 48$ nm. The particle size of the ZnO nanopowder in this porous architecture is also counter ion dependent. With the same synthesizing process by using nitrate ($\text{Zn}(\text{NO}_3)_2$) instead of sulfate as the zinc source. The ZnO particle size obtained at 450 °C is $D_{\text{BET}} = 71$ nm, i.e. twice of that from the ZnSO_4 precursor. This has also been corroborated by Raj et al., in which ZnO nanopowder with similar architecture but larger crystalline and particle sizes were obtained from zinc chloride salt and oxalic acid at 500 °C.

This porous ZnO architecture is precursor dependent as demonstrated by the SEM in Fig. 5a. The micrograph of the oxalate precursor exhibits an identical rectangular shape. During the calcination process, the initial pore in the precursor is formed by the release of the two water molecules (Reaction (1)). Hence, the pore volume further increased for $T \geq 350$ °C with the subsequent release of CO_2 and CO from the precursor (Reaction (2)), the simultaneous nucleation and growth of ZnO primary particles. This is in good agreement with the work of Jia et al. [11].

4. Conclusion

ZnO nanopowders with porous architecture were synthesized by a simple and inexpensive method. This method consists of 1) precipitation of metastable orthorhombic zinc oxalate dihydrate ($\beta\text{-ZnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$) in a hydro alcoholic solution from zinc salt and oxalic acid at room temperature, 2) its dehydration into monoclinic anhydrous zinc oxalate ($\beta\text{-ZnC}_2\text{O}_4$) at 125 °C and 3) decomposition into zinc oxide nanopowder at 350 °C. Detailed crystalline parameters for each of the species were analyzed and the phase transition mechanisms between different structures were shown in detail by high temperature XRD coupled with TGA analysis in the temperature range of RT–450 °C. From the XRD, SEM and BET analysis, it was confirmed that the resultant

ZnO porous architecture consists of a large number of homogeneous nanometric spherical zinc oxide particles with a pure hexagonal wurtzite structure, confined in a sub-micronic rectangular shape. The particle size of the ZnO nanopowder has been proven to be temperature and counter ion dependent. In this synthesis, ~13 to 20 nm spherical ZnO particles with a 53 m²/g specific surface could be easily obtained, rendering it a very interesting candidate as a photo catalyst and for photovoltaic application.

Acknowledgments

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