Structural and vibrational properties of hydrothermally grown ZnO$_2$ nanoparticles

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1. Introduction

The novel physical properties exhibited by the nanomaterials have stimulated an exhaustive research concerning growing methods which allow scientist to control the morphology, size and chemical composition of these materials, and consequently, their resulting physical properties. In this regard, relevant progress has been achieved on the synthesis of semiconductors nanocrystals and the study of their physical properties.

Among semiconductors, nanostructured zinc oxide (ZnO) has been recognized as a promising material for applications in solar-cells [1], field emission [2], gas sensing [3], light emitting devices [4,5], and catalysis [6–8]. However, growing nanostructured ZnO through physical methods like sputtering [9,10], vapor–liquid–solid [11], epitaxial growth [12,13], or ablation laser [14,15], among others techniques, commonly requires expensive equipments; on the other hand, chemical routes to synthesize ZnO nanostructures frequently involve toxic reactants used as surfactants to control the nucleation and growing process.

Zinc peroxide (ZnO$_2$) has been identified as a potential green precursor to obtain ZnO nanostructures at low temperatures. Here, it is reported the synthesis of ZnO$_2$ nanoparticles through an economical one step hydrothermal method. The thermal stability, morphology, structural and vibrational properties of the ZnO$_2$ nanoparticles were studied by means of thermogravimetry/differential scanning calorimetry, X-ray diffraction, low- and high-resolution transmission electron microscopy, infrared spectroscopy and Raman spectroscopy. Highly crystalline cubic-ZnO$_2$ nanoparticles with average size of 15 nm were obtained. It was found that the synthesized ZnO$_2$ sample decomposes into ZnO at about 250 $^\circ$C. The observed vibrational modes in the ZnO$_2$ nanopowder are discussed and compared with previous reports.

2. Experimental section

The following chemicals were purchased and used without further purification: zinc acetate dihydrate [Zn(CH$_3$COO)$_2$·2H$_2$O; 99.6%, Baker] and hydrogen peroxide [H$_2$O$_2$; sol. 30%, Baker].
In a typical synthesis of ZnO₂ nanoparticles 80 ml of a zinc acetate solution 0.033 M was mixed with 4 ml of hydrogen peroxide in a boiling flask under vigorous stirring. Then the solution was heated up to 100 °C and kept at this temperature for 10 h. At this stage it was observed that the appearance of the solution progressively turns from translucent to cloudy white, indicating the formation of the nanoparticles. Finally, the solution was cooled freely to room temperature; then the solid material was extracted by centrifugation and washed several times with deionized water.

The sample was characterized using X-ray diffraction (XRD; Bruker Advance D-8), transmission electron microscopy (TEM; Philips Tecnai F20, 200 kV), thermogravimetry/differential scanning calorimetry (TGA/DSC; Nalitek, STA 449 F3 Jupiter), the Fourier transform infrared spectroscopy (FT-IR; Escalibur Series Digilab FTS 3000X), and room temperature Raman spectroscopy in backscattering configuration using the 633 nm line of a He–Ne laser as excitation source (LabRAM HR-Olympus Micro Raman system).

The XRD pattern of the sample was obtained using a X-ray radiation with wavelength of 1.5418 Å (CuKα), setting the step width and step counting time at 0.02° and 4.0 s, respectively. To obtain further details of crystalline structure of the nanoparticles Rietveld method was performed by means of FULLPROF98 software [30] using pseudo-Voigt functions to fit the diffraction peaks [31]. The Rietveld refinement procedure included the variables related to scale factor, atom fractional coordinates, lattice parameters, isotropic thermal displacements, crystallite shape and size, and lattice strain.

3. Results and discussion

Fig. 1 shows the experimental XRD pattern of the powder sample. The X-ray pattern reveals that the sample is constituted by crystallites of cubic-ZnO₂ with space group Pa3̅ (no. 205). The entire diffraction peak positions match with that reported for cubic-ZnO₂ powders [32]; no XRD peaks besides those related to ZnO₂ phase were detected. It can be noted that although the XRD pattern shows strong X-ray reflections, a slight broadening is also observed, suggesting that the sample is composed by ZnO₂ nanocrystallites with high crystal quality.

In order to study in further detail the crystal structure of the synthesized ZnO₂ nanocrystallites, Rietveld refinement procedure was performed (Fig. 1). Table 1 summarizes the obtained refined parameters for the powder sample. It was found that the parameter related to the crystallite size was about 15 nm, in agreement with the estimated average size using the Scherer’s equation [33] (20 nm).

Fig. 2 presents a model of the optimized unit cell of ZnO₂. It can be seen that the cubic-ZnO₂ structure is constituted by an array of irregular octahedra formed by a Zn ion (Zn²⁺) at the center surrounded by four O ions (O⁻) located one at each corner of the polyhedron (Fig. 2b). It is worth to note that in the cubic-ZnO₂ lattice the interatomic distance between oxygen ions can be as short as 1.47 Å, 0.64 Å less than the Zn–O bond length for the same atomic array (2.11 Å). Such structural feature provides sites where the local charge balance is not preserved, leading to structural instability as temperature increases. It follows the characteristic low decomposition temperature of ZnO₂ compound (~240 °C) [18,23,34–37] as compared with ZnO (>1500 °C) [38], or even some zinc carboxylates like zinc acetate (~270 °C) [39–41]. It is proposed that the formation mechanism of the hydrothermally grown ZnO₂ nanoparticles is by the following chemical reactions:

\[
\begin{align*}
Zn(CH₃COO)₂ · 2H₂O & \rightarrow Zn²⁺ + 2(CH₃COO)^⁻ + 2H₂O, \quad (1) \\
CH₃COO⁻ + H₂O & \rightarrow CH₃COOH + OH⁻. \quad (2) \\
Zn²⁺ + 2OH⁻ & \rightarrow Zn(OH)₂, \quad (3) \\
Zn(OH)₂ + H₂O₂ & \rightarrow ZnO₂ + 2H₂O, \quad (4) \\
2H₂O₂ & \rightarrow 2H₂O + O₂ \quad (5)
\end{align*}
\]

Eq. (1) states the decomposition of the zinc acetate in aqueous media into Zn²⁺ and acetate ions. Since the CH₃COO⁻ ion is a strong base it is expected that it can be readily protonized to produce acetic acid and hydroxyl radicals (Eq. (2)). It is well know that the metal ions in the alkaline solutions get surrounded by OH⁻ ions to form hydroxides of different aggregation states.

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**Fig. 2.** (a) Refined unit cell model and (b) array of octahedron building blocks for cubic-ZnO₂ structure.

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Refined cell parameters, calculated average particle size and maximum strain.</th>
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<tr>
<td>Space group</td>
<td>Cell parameter  (Å)</td>
</tr>
<tr>
<td>Pa3 (No. 205)</td>
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**Fractional atomic positions**

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<tr>
<th>Atom</th>
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<th>y</th>
<th>z</th>
</tr>
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<tr>
<td>Zinc</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Oxygen</td>
<td>0.4132(2)</td>
<td>0.4132(2)</td>
<td>0.4132(2)</td>
</tr>
</tbody>
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form metallic hydroxides units [M(OH)ₓ] (Eq. (3)); we proposed that this intermediate compound reacts with hydrogen peroxide to form the ZnO₂ seeds (Eq. (4)); last chemical reaction involves the decomposition of hydrogen peroxide, the formation of the strong oxidizer ion O₂²⁻ and release of oxygen gas (Eq. (5)). From Eq. (4), it is worth to note that in order to transform all the content of zinc hydroxide into ZnO₂ it is necessary to add an equimolar amount of H₂O₂; it follows that while lower amounts of hydrogen peroxide may lead to obtain traces of zinc salts mixed with ZnO₂ phase, higher concentrations of H₂O₂ only result in the increase of the amount of released oxygen gas; nevertheless it could modify the crystal growth kinetics.

In order to study further the atomic arrangement and the morphology of ZnO₂ nanocrystals, low and high resolution TEM were used. Fig. 3 presents a typical low resolution TEM image of the ZnO₂ nanoparticles. Although the particle size cannot be precisely determined from this image, it is possible to distinguish some nearly spherical nanoparticles with diameters ranging from 10 to 15 nm (marked with circles). The inset of this figure shows a HR-TEM image of a crystalline ZnO₂ nanoparticle; the interplanar spacings corresponding to the (2 0 0) and (1 1 1) planes (0.246 and 0.282 nm, respectively) of the cubic-ZnO₂ structure are well resolved.

Since the potential use of ZnO₂ nanopowder to obtain ZnO products through thermal decomposition depends on the use of low reaction temperatures, thermogravimetry/differential scanning calorimetry characterization was performed to the ZnO₂ nanopowder. Fig. 4 shows the thermal analysis of the sample. A strong weight loss (71.3%) is detected about 250 °C, which is attributed to the thermal decomposition of ZnO₂ into ZnO, following the exothermic reaction

\[ 2\text{ZnO}_2 \rightarrow 2\text{ZnO} + \text{O}_2 \]  

Besides the exothermic peak located at 250 °C, another thermal signal appears at about 263 °C along with a 2.4% in weight loss; such process might be associated with either the decomposition of remaining organic products (CH₃COOH) adsorbed on the surface of the ZnO₂ nanoparticles or the decomposition of un-reacted precursor, like zinc acetate [42]. Last assumption is better supported, since the exothermic signal agrees with the reported decomposition temperature for this compound [39–41]. The Eq. (7) states the thermal decomposition of zinc acetate into ZnO, carbon dioxide and water.

\[ \text{Zn(CH}_3\text{COO)}_2 + 4\text{O}_2 \rightarrow \text{ZnO} + 4\text{CO}_2 + 3\text{H}_2\text{O} \]  

No evidence suggesting the presence of Zn(OH)₂ traces in the sample was found by neither thermal analysis nor infrared spectroscopy (discussed below).

It is worth to note that the weight loss due to the thermal decomposition of zinc peroxide into zinc oxide is considerably larger than the expected theoretical value of 16.4%. The observed weight loss of 71.3% cannot be explained just by oxygen release; however, it may be attributed to some ZnO nanoparticles carried out from the porcelain boat after the thermal decomposition of ZnO₂ nanostructures by the gas flow used to obtain the protective atmosphere. Similar TGA curves were observed by Cheng et al. [36] in their thermogravimetric analysis; they observed a weight loss of 89.5% at 229 °C for their ZnO₂ samples.

The mid-infrared spectrum of the ZnO₂ sample is shown in Fig. 5a. The following infrared absorption bands are well resolved: 3416, 2924, 2853, 2116, 1649, 1578, 1410, 1346, and 1028 cm⁻¹; additionally a strong band with wavenumber lower than 500 cm⁻¹ is recognized. The bands at 3416, 2116 and 1649 cm⁻¹ are attributed to the stretching, rocking + bending and bending modes of water molecules [43] adsorbed on the surface of the ZnO₂ nanoparticles, respectively. It is worth to note that the measured infrared spectrum of the sample has strong similarities with that reported for zinc acetate [44], suggesting the presence of un-reacted zinc precursor, in agreement with the TGA/DSC analysis. The weak bands at 2924 and 2853 cm⁻¹ are located in the characteristic frequency range of stretching modes of C–H bonds [44,45]; corresponding to the antisymmetric and symmetric modes of the −CH₃ group, respectively. The bands located at 1578, 1410, 1356 and 1028 cm⁻¹ could be assigned to the stretching mode of −COO, two bending modes and a rocking mode of −CH₃ groups of zinc acetate units, respectively [44].

Cheng et al. [36] have reported infrared absorption bands located at about 1420, 1334 and 1040 cm⁻¹ for their hydrothermally grown ZnO₂ samples, all of them attributed to vibrational modes of peroxy ions (O₂²⁻). However, in their IR spectra it is

Fig. 3. Typical low resolution TEM image of ZnO₂ nanoparticles agglomerates. Inset: HR-TEM image showing the interplanar spacing corresponding to (2 0 0) and (1 1 1) planes of a ZnO₂ nanoparticle.
observed that the band at 1040 cm\(^{-1}\) remains at temperatures as high as 500 °C, suggesting that absorption due to O\(_2^2^-\) is not the origin. On the other hand, the bands at 1420 and 1334 cm\(^{-1}\) almost disappear at the same temperature. An overlap of the bands attributed to the bending modes of \(-\text{CH}_3\) group of zinc acetate with those of O\(_2^2^-\) ions can explain the observed strong absorption intensity in our spectrum. Finally, the infrared band with wavenumber lower than 500 cm\(^{-1}\) is attributed to Zn–O bond; similar strong absorption band located at 429 cm\(^{-1}\) for ZnO\(_2\) samples has been already reported [38].

The Raman spectrum of the ZnO\(_2\) powder is shown in Fig. 5b. A strong peak centered at 835 cm\(^{-1}\) is well resolved; besides two weak peaks located at 407 and 483 cm\(^{-1}\) are observed. Sun et al. [18] reported similar Raman peaks located at about 410 (medium), 470 (weak), 840 (strong), and 930 cm\(^{-1}\) (weak) for their ZnO\(_2\) samples; however, no tentative assignment was provided. Others authors have also reported a Raman peak for ZnO\(_2\) nanoparticles located at 840 cm\(^{-1}\), which was attributed to the stretching mode of the O–O bond of the peroxo ion (O\(_2^2^-\)) [34]. Analogous Raman active modes have been detected in inorganic peroxide compounds like BaO\(_2\) (838 cm\(^{-1}\)) attributed to vibration of the O–O bond [46].

Since the ZnO\(_2\) unit cell has an inversion center the rule of mutual execution applies [47]; then a vibrational mode cannot be both Raman and infrared active. The bands at 1410, 1356, 835, and 429 cm\(^{-1}\) fulfill this rule; however, in order to support the provided assignments comparisons with theoretical calculations of the phonon branches for ZnO\(_2\) are desirable; nevertheless, to the best of our knowledge, such studies are not available yet.

4. Conclusions

High crystalline cubic phase ZnO\(_2\) nanoparticles with average size of 15 nm can be synthesized through one step hydrothermal route. Their thermal decomposition at 250 °C makes ZnO\(_2\) a potential green precursor to obtain ZnO nanostructures at low temperatures. It is found that the infrared band at about 1040 cm\(^{-1}\) reported for ZnO\(_2\) is not related to some vibrational mode of O\(_2^2^-\) ion, instead it is proposed that it has as origin an adsorbed or unreacted precursor. On the order hand, the Raman active mode with frequency of 835 cm\(^{-1}\) seems to be a characteristic of crystalline peroxide compounds.

Acknowledgments

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References
