Synthesis and characterization of spherical and narrow size distribution indium oxide nanoparticles

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1. Introduction

It is generally known that nanostructured materials display unusual physical properties that differ from those of bulk materials and are promising for the fabrication of novel devices [1]. In recent years, a wide range of nanosized powders have been synthesized to engineer desired properties such as chemical, electrical, mechanical and optical properties.

Transparent conducting oxides (TCOs) have been extensively studied due to their diverse technological applications. Indium oxide (In₂O₃), a wide band gap (~3.6 eV) [2] transparent semiconductor, is of great interest for many device applications due to its unusual combination of high transparency in the visible region and high electrical conductivity when prepared under special conditions [3]. Currently, indium oxide-based materials are used in electrooptic modulators, in the electronic field as window heater, solar cells, electrochromic mirrors, and flat-panel displays.

In addition, nanostructures based on indium oxide are promising device materials for chemical sensors and in the upcoming nanoelectronic building blocks [4–6].

Several methods, comprising all three phases, namely, the solid phase, the solution phase, as well as the vapor phase, have been used for the preparation of In₂O₃ powders and thin films [4,7–18]. It is generally known from literature reports [19,20] that nanostructured materials are influenced by shape, size and size distribution of small units, which in turn depend on the characteristics of synthesis.

In this work, In₂O₃ nanoparticles were synthesized by a surfactant-free room temperature soft chemistry route. Spherical indium oxide nanoparticles (about 8 nm in diameter) were obtained after thermal treatment of gels at 400 °C for 2 h, as shown by X-ray diffraction experiments and nitrogen adsorption measurements. Transmission electron microscopy observations confirm the single-crystalline nature of the produced nanoparticles. The photoluminescence emission spectrum at room temperature shows a broad peak with onset at approximately 315 nm as a result of quantum size effect as revealed by small-angle X-ray scattering.

2. Experimental

Indium oxide (99.99%, Aldrich) and hexamethylenetetramine, HMT ((CH₂)₆N₄ 99%, Alfa Aesar) were used as starting materials without further purification. A stock solution (0.04 mol L⁻¹, pH 1) of indium nitrate was prepared by dissolving In₂O₃ in nitric acid
and deionized water under heating and stirring. In a previous investigation [21] it was shown that the use of indium nitrate and indium chloride gave rise to nanosized indium oxide nanoparticles. However, indium nitrate is preferred because of the smallest size of the produced powder material. An excess HMT solution (0.5 mol L\(^{-1}\)) was added dropwise to the indium salt solution at room temperature, and maintained under stirring for 24 h for precipitation completion. During this process, the HMT slowly hydrolyzes to yield ammonia and formaldehyde. No high temperature aging was performed to avoid crystal growth. The resulting dispersion was filtered through a 0.2 \(\mu\)m membrane, and the recovered precipitate was washed twice with isopropyl alcohol. The washed precipitate was dried overnight in air at 40 °C. The yield was about 70% of the amount that could be extracted if all indium ions in solution would precipitate during the reaction.

In a conventional precipitation experiment, an external precipitant agent added to a solution containing the metal cation of interest would produce the precipitation of the oxide cation or of a precursor material. In the homogeneous precipitation method the precipitating agent is generated in situ and the formation of nuclei occurs thoroughly in the reaction medium minimizing concentration gradients. In this case, the diffusion rate of monomer species responsible for the formation of nuclei is the same in the whole reaction volume and the precipitates are generated simultaneously and uniformly throughout the solution. This procedure allows for obtaining a good control over the precipitate shape and size. In addition, a narrow distribution of particle size should be expected.

The thermal decomposition behavior of the indium precipitate was studied by simultaneous thermogravimetry, TG, and differential thermal analysis, DTA (Netzsch, STA 409) under flowing (50 mL min\(^{-1}\)) synthetic air with heating rate of 5 °C min\(^{-1}\). Fourier transform infrared spectroscopy, FTIR (Nicolet, Magna IR 560) analysis in the spectral range 400–4000 cm\(^{-1}\) was carried out to obtain a better insight into the constitution of the precipitate and thermally decomposed materials. Powder materials were mixed to KBr for this analysis. The specific surface area, \(S\), of thermally decomposed powders was analyzed using five-point Brunauer, Emmett and Teller (BET) method by nitrogen adsorption (Micromeritics, ASAP 2010) after degassing at 300 °C. X-ray diffraction patterns were recorded using a diffractometer (Bruker-AXS, D8 Advance) with a \(0–2\theta\) Bragg-Brentano configuration, operating at 40 kV and 40 mA with a Ni-filtered Cu-K\(\alpha\) radiation. The crystallite size was estimated by the line broadening method. The shape of the diffraction peaks was assumed to be represented by a Gaussian function and high-grade Si powder was used as standard material for the instrumental broadening correction. The morphology of powder materials was examined by transmission electron microscopy (Philips, CM 200). Photoluminescence, PL, emission spectra were recorded at room temperature, collected at an angle of 22.5° (front face) in a spectrofluorimeter (SPEX, Fluorolog 2) with double grating 0.22 mm monochromator (Spex 1680) and using a 450 W Xenon lamp as the excitation source.

Small-angle X-ray scattering experiments were carried out at the SAXS beamline of the Brazilian National Synchrotron Light Laboratory (LNLS). Data were collected in transmission mode geometry, with incident wavelength \(\lambda = 1.608\) Å at a sample to detector distance equal to 845 mm, allowing for measurements of the scattered radiation in the range of scattering vector, \(q\), from 0.013 to 0.344 Å\(^{-1}\) (where \(q = (4\pi/\lambda) \sin\theta\), being \(\theta\) half of the scattering angle). Details of the experimental setup of the SAXS beamline at the LNLS can be found elsewhere [22]. All SAXS data were corrected for parasitic scattering and sample attenuation. Experimental data were fitted using the GNOM software [23].

### 3. Results and discussion

Small amount of the as-prepared material was dispersed in distilled water, spread over a carbon film on a TEM-grid and observed in transmission electron microscope. The TEM micrograph of Fig. 1 shows that the as-prepared indium hydroxide consists of highly agglomerated nanosized particles with irregular shape. The larger particles have a rod-like shape ~20 nm long. The selected area electron diffraction (SAED) pattern of the nanoparticles is consistent with the cubic structure of indium hydroxide. Only one ring is clearly visible in the SAED pattern indicating a preferential growth of the crystallites along a (2 0 0) plane or that the crystallites are stacked together along that direction.

Fig. 2 shows the thermal decomposition behavior of the as-prepared material. The experimental weight loss in the TG curve is 18.5% up to 350 °C, and beyond this temperature it is negligible. The thermal decomposition of indium hydroxide to give indium oxide results in 16.7% weight loss. The DTA curve exhibits two endothermic peaks at 128 and 216 °C. The former is associated with the elimination of physisorbed water, and accounts for the

![Fig. 1. Bright-field TEM micrograph and selected area diffraction of the as-prepared material.](image)
The XRD pattern after thermal treatment of the hydroxide method for the (2 0 0) reflection in the precursor material is 16 nm, according to ICDD file 88-2160 of cubic bixbyite-type In$_2$O$_3$ (space group Ia$ar{3}$). The decomposition reaction, the diffraction pattern was indexed (In(OH)$_3$, cubic, space group Im$ar{3}$), which may be assigned to crystalline indium hydroxide peaks, which may be assigned to crystalline indium hydroxide (In(OH)$_3$, cubic, space group Im$ar{3}$) according to ICDD-76-1463. The observed reflections at 22.3° and 45.4° assigned to (2 0 0) and (4 0 0) planes, respectively, indicate a preferential growth of crystallites along the (2 0 0) plane, in agreement with TEM results. In general, the shape of nanostructured materials depends on the method of synthesis. Rod-like nanoparticles of In(OH)$_3$ have been obtained in powders prepared by high temperature hydrolysis of indium chloride [24]. In general, the shape of nanostructured materials depends on the method of synthesis. Rod-like nanoparticles of In(OH)$_3$ have been obtained in powders prepared by high temperature hydrolysis of indium chloride [24].

The average crystallite size estimated by the line broadening method for the (2 0 0) reflection in the precursor material is 16 nm. The XRD pattern after thermal treatment of the hydroxide precursor at 400 °C for 2 h (Fig. 3b) reveals the completion of the decomposition reaction. The diffraction pattern was indexed according to ICDD file 88-2160 of cubic bixbyite-type In$_2$O$_3$ (space group Ia$ar{3}$). The average crystallite size estimated for the most intense (2 2 2) reflection is 8 nm evidencing that nanoparticles of indium oxide may be easily formed by this method of synthesis. It is worth noting the lower size of the indium oxide nanoparticles compared to that of the precursor indium hydroxide. This decrease in the size of nanoparticles might produce an increase in the density of surface states (surface defects). The absence of any preferred orientation in the thermally treated powder indicates that the shape of the precursor material (indium hydroxide) was not preserved.

The specific surface area determined by the BET method after thermal treatment of indium hydroxide at 400 °C for 2 h is 107 m$^2$ g$^{-1}$. This rather high value is an evidence of the nanosize nature of the synthesized material. An estimation of the particle size, $d_{BET}$, may be obtained from this result assuming a spherical shape for the nanoparticles, by the equation: $S = 6/\rho d_{BET}$, where $\rho$ is the crystallographic density of In$_2$O$_3$ [7.18 g cm$^{-3}$]. The calculated value (7.8 nm) matches the average crystallite size determined by X-ray diffraction, which ensures that the produced particles are spherical in shape and suggesting that each nanoparticle is composed by one crystallite (or primary particle).

As a consequence of the high specific surface area of indium oxide nanoparticles, several In$^{3+}$ ions may be found in the hydrophilic surface of the oxide [25]. In this case, hydrogen bonds may occur among hydroxyl groups or water molecules adsorbed on the surface of nanoparticles. Fig. 4 shows FTIR spectra of the as-prepared (a) and thermally treated (b) materials. In these spectra absorption bands at ~1385 and ~1640 cm$^{-1}$ are assigned to nitrate groups and bend deformation of water, respectively. Other absorption bands at ~3450, ~3200, ~3100, and ~2900 cm$^{-1}$ are due to metal–oxygen bonds. These results are in general agreement with those of thermal analysis.

The morphology of In$_2$O$_3$ was observed by TEM. The bright-field image shown in Fig. 5 confirms that nanoparticles are spherical in shape and the distribution of particle size is relatively narrow. The average size of nanoparticles estimated from TEM micrographs (~8 nm) is in close agreement with that obtained from XRD line broadening analysis, which supports the formation of single-crystalline indium oxide nanoparticles. Multiple rings are seen in the SAED spectrum, as expected from the XRD pattern (Fig. 3b).

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It is well known from the literature [26] that conventional micronsized In$_2$O$_3$ cannot emit light at room temperature, whereas photoluminescence emissions have been observed in thin films and nanostructures [10,13,17,27–29]. The origin of photoluminescence in In$_2$O$_3$ has been attributed to different effects, and the mechanism is still not clear. At lower energies (~400 to ~520 nm) PL peaks have been related to amorphous indium oxide or oxygen vacancies [17,28,29] and more recently to indium interstitials and their associated complex defects [30], whereas at higher energies (~<350 nm) it has been assigned to a quantum size effect [10,13,27].
The PL spectrum (excitation at 250 nm) obtained at room temperature for In$_2$O$_3$ shown in Fig. 6, reveals a broad emission peak with onset at ~315 nm, which is blue-shifted compared to the 338 nm of bulk commercial indium oxide [10].

In this case, the PL emission peak of In$_2$O$_3$ nanoparticles suggests a quantum size effect, taking into account the spectral region of the PL emission peak. However, regarding results of FTIR (Fig. 4), the surface of nanoparticles is highly active as confirmed by the presence of hydroxyl groups. In a high active surface several types of defects are expected to be found. These defects are expected to give rise to oxygen vacancies and other point defects in indium oxide nanoparticles, although the characteristic photoluminescence emission spectrum would be expected to occur at higher wavelengths (blue–green region).

The quantum confinement effect is primarily dependent on the particle size, which is expected to occur as that value approaches the exciton Bohr diameter (about 2.6 nm for In$_2$O$_3$ [31]). In this case a general agreement among the average particle size values determined from XRD, BET and TEM (~8 nm) may be noticed. However, the average particle size determined from these techniques is too large to account for a quantum confinement effect. In this regards, it should be noted that all these characterization techniques have some limitation. These techniques are suitable to analyze small size particles, but in some instances none of them can describe the true particle size distribution. XRD and BET results give an average value over a population of particles, whereas the size distribution obtained by TEM can be unreliable due to contrast and/or agglomeration problems [32].

In order to obtain a further insight in structural and microstructural characteristics of In$_2$O$_3$ nanoparticles, small-angle X-ray scattering measurements were carried out. The SAXS technique allows for obtaining structural information about fluctuations of the electronic density within a specific sample, with a characteristic length on the order of approximately 1–100 nm. It is, therefore, a suitable technique to give information on the size, shape and size distribution of the particles in the nanoscale. The scattering curve of indium oxide nanoparticles is shown in Fig. 7. The experimental scattering profile (open symbol) was fitted (line) assuming a polydisperse system of spherical particles [33]. The calculation results did not converge when attempting to fit the experimental data to a monodisperse system model.

The scattered X-ray intensity $I(q)$ for a system consisting of polydisperse particles within a matrix with a contrast in its


where \( g(R) \) is the distribution of particle sizes and
\[ f_{q_{\text{max}}}^{q_{\text{min}}} g(R) v(R) dR = N(R), \]
with \( N(R) \) the density of particles per unit volume, \( v(R) \) is the volume occupied by particles of dimension \( R \), and \( f(q, R) \) is a geometrical factor [34].

The volumetric size distribution function given by:

\[ D_v(R) = g(R) v(R) \tag{2} \]

can be calculated from the scattering curve assuming a distribution of spherical particles.

The scattering curve (Fig. 7) seems to contain the contributions of two different scattering components. One of them consists of a low \( q \) rise, and the other component predominates in the intermediate and high \( q \) regions. These two components are separated by a curved crossover region suggesting that the low \( q \) component is related to \( \text{In}_2\text{O}_3 \) agglomerates. This low \( q \) component was neglected in the fitting. In the intermediate and high \( q \) domain, which corresponds to short length scales, the fitted curve exhibits a power law with an exponent equal to \(-4\). This slope corresponds to Porod’s model indicating that the system is composed by spherical particles with sharp and smooth interfaces [35].

Fig. 8 shows the volumetric size distribution function
\[ D_v(R) = \left( \frac{4\pi}{3} \right) R^2 N(R). \]

This curve allows for determination of the volume weighted particle size distribution, which varies from \( 2R = 1.5 \) to 12 nm. Therefore, a very narrow particle size distribution was obtained with this method of synthesis, corroborating TEM observations (Fig. 5). The volumetric size distribution curve consists of two populations. The larger population component has a maximum amplitude at \( 2R = 7.15 \) nm, whereas the small population component is centered approximately at \( 2R = 2.8 \) nm. The former agrees, within experimental limitations, with those values obtained by X-ray diffraction, nitrogen adsorption and TEM. The latter population of nanoparticles is believed to be responsible for the quantum size effect giving rise to the weak room temperature photoluminescence emission, since it is in close agreement to the exciton Bohr diameter.

4. Conclusions

Spherical and single-crystalline \( \text{In}_2\text{O}_3 \) nanoparticles with predominant average size \( \sim 8 \) nm were successfully prepared by a surfactant-free room temperature homogeneous precipitation method. The simple and cost-effective method of synthesis is useful for practical applications of this material whenever a narrow distribution of particle size is required. The rod-like shape of the precursor material changed to spherical nanoparticles with thermal treatment at 400 °C. The prepared powder exhibits a weak and broad photoluminescence emission in the blue–UV region due to a quantum size effect. This result is attributed to a small population of nanoparticles with average size lower than 3 nm as demonstrated by SAXS experiments, which proved to be a suitable technique for the analysis of particle size distribution in the very low size range.

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References

[30] C. The prepared powder exhibits a weak and broad photoluminescence emission, since it is in close agreement to the exciton Bohr diameter.

Fig. 8. Volumetric size distribution function calculated from the fitted experimental SAXS curve.