Indium oxide (In$_2$O$_3$) nanoparticles using Aloe vera plant extract: Synthesis and optical properties

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In$_2$O$_3$ nanoparticles with particle sizes of 5-50 nm were synthesized by a simple, cost effective and environmental friendly route using indium acetylacetonate and Aloe vera plant extracted solution. The precursor was characterized by TG-DTA to determine the thermal decomposition and crystallization temperature which was found to be at above 350 °C. Nanoparticles are formed after calcination the dried precursor of In$_2$O$_3$ in air at 400-600°C for 2 h. Structural, morphological and optical properties of the synthesized nanoparticles were characterized. XRD and TEM analysis showed that the In$_2$O$_3$ samples are cubic with particle sizes of 5-50 nm. The morphology and size of In$_2$O$_3$ materials were affected by the calcination temperature. The prepared In$_2$O$_3$ nanoparticles showed a strong PL emission in the UV region. The strong emissions of In$_2$O$_3$ are attributed to the radioactive recombination of an electron occupying oxygen vacancies with a photo-excited hole. The present work proves that the Aloe vera plant-extracted solution synthesis is a new useful method using cheap precursors for preparation of In$_2$O$_3$ nanoparticles.

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1. Introduction

Indium oxide (In$_2$O$_3$) is an important n-type semiconductor with wide direct band-gaps of 3.35-3.75 eV. It has interesting properties such as high transparency to visible light, high electrical conductance, and strong interaction between certain poisonous gas molecules and its surfaces [1-3]. These properties make In$_2$O$_3$ an interesting material for a variety of applications, including solar cells [1,2], panel displays [4], organic light emitting diodes [5], photocatalysts [6], architectural glasses [7], field emission [8]. Moreover, In$_2$O$_3$ is an important material for semiconductor gas sensors [9-14]. Recently, investigations on preparation of In$_2$O$_3$ nanostructures with various forms such as nanotubes [15], nanobelts [16-18], nanofibers [19,20], wires [21-28], and nanoparticles [29-31] have been widely emphasized to extend their technological applications. Among these nanostructures, In$_2$O$_3$ with nanoparticulate form has been intensively studied to be used as a promising material for gas sensor applications. So far, nanoparticles of In$_2$O$_3$ have been synthesized by several techniques including sol–gel technique [9,12,32], pulse laser deposition [29], thermal decomposition [30,33,34], thermal hydrolysis [35], microemulsion [31,36], spray pyrolysis [37], mechanical chemical processing [38], hybrid induction and laser heating (HILH) method [39], nonaqueous synthesis [40], and hydrothermal synthesis [41]. Among other established synthesis methods, simple and cost effective routes to synthesize nanocrystalline In$_2$O$_3$ by utilization of cheap, nontoxic and environmentally benign precursors are still the key issues.

Aloe vera (Aloe barbadensis Miller) is a perennial succulent belonging to the Liliaceal family, and it is a cactus-like plant that grows in hot, dry climates [42]. For many years, aloe vera has been reported to possess immunomodulatory, anti-inflammatory, UV protective, antiprotozoal, and wound- and burn-healing promoting properties [43-46]. Recently, the extract of Aloe vera plant has been successfully used to synthesize single crystalline triangular gold nanoparticles (~50-350 nm in size) and spherical silver nanoparticles (~15 nm in size) in high yield by the reaction of aqueous metal source ions (chloroaurate ions for Au and silver ions for Ag) with the extract of the Aloe vera plant [47]. To the best of our knowledge, this biosynthetic route has not been extended to the preparation of oxide materials.

Here, we report for the first time the novel synthesis of In$_2$O$_3$ nanoparticles with particle sizes of 5-50 nm using indium acetylacetone and Aloe vera plant extracted solution. Nanoparticles are formed after calcination the dried precursor of In$_2$O$_3$ in air at 400-600°C for 2 h. This method utilizes Aloe vera plant extracted solution as a solvent instead of organic solvents. The advantages of this method include (i) use of cheap, nontoxic and environmentally benign precursors and (ii) simple procedures without time-consuming polymerization and problem with treatment of a highly viscous polymeric
resin. The current simple synthetic method using cheap precursors of Aloe vera plant extract provides high-yield nanosized materials with well crystalline structure and good optical properties, and the method can be used to prepare nanocrystalline oxides of other interesting materials.

2. Experimental

In this study, indium (III) acetylacetonate (99.99% purity, Aldrich) was used as the starting chemical material for In$_2$O$_3$. Aloe vera extracted solution was prepared from a 35 g portion of thoroughly washed Aloe vera leaves which were finely cut and boiled in 100 ml of de-ionized water. The resulting extract was used as an Aloe vera extract solution. In the preparation of In$_2$O$_3$ nanoparticles, 3 g of indium (III) acetylacetonate was first dissolved in 30 ml Aloe vera extract solution under vigorous stir at 60°C for several hours until dried. The dried precursor was crushed into powder using mortar and pestle. The precursor was characterized by X-ray diffraction (XRD) using a Philips X-ray diffractometer (PW3040, The Netherlands) with CuK$_\alpha$ radiation ($\lambda = 0.15406$ nm). The particle size and morphology of the calcined powders were characterized by transmission electron microscopy (TEM, Hitachi H8100 200 kV) to determine the thermal decomposition and crystallization temperature which was found to be at above 350°C (Fig. 1). The dried precursor was ground and subsequently calcined in box-furnace at 400, 500, and 600°C for 2 h in air. The dried precursors and calcined samples of In$_2$O$_3$ were characterized for crystal phase identification by powder X-ray Diffraction (XRD) using a Philips X-ray diffractometer (PW3040, The Netherlands) with CuK$_\alpha$ radiation ($\lambda = 0.15406$ nm). The particle size and morphology of the calcined powders were characterized by transmission electron microscopy (TEM, Hitachi H8100 200 kV). The optical absorption spectra were measured in the range of 200-800 nm using a UV-3101PC UV-VIS-NIR scanning spectrometer (Shimadzu, Japan). Photoluminescence (PL) measurement was carried out on a luminescence spectrometer (Perkin–Elmer LS-55B, PerkinElmer Instrument, USA) using a Xenon lamp as the excitation source at room temperature. The samples were dispersed in dichloromethane and the excitation wavelength used in PL measurement was 250 nm.

3. Results and discussion

The thermogravimetric-differential thermal analysis (TG-DTA) curves of as-prepared In$_2$O$_3$ precursor are shown in Figure 1. The TG curve in Figure 1 shows a major weight loss step from 190°C up to about 350°C with slightly weight loss from 350°C to 600°C, and no further weight loss was observed at above 600°C. The weight loss is related to the combustion of organic matrix. On the DTA curve (Figure 1) a main exothermic effect was observed between 260°C and 360°C with a maximum at about 320°C, indicating that the thermal events can be associated with the burnout of organic species involved in the precursor powders (organic mass remained from Aloe vera extract), of the residual carbon or due to direct crystallization of nanocrystalline In$_2$O$_3$ from the amorphous component. The formation of nanocrystalline In$_2$O$_3$ as decomposition product was confirmed by XRD and Raman results shown in Figure 2 and 3. The XRD patterns of In$_2$O$_3$ samples are show in Figure 2. All of the detectable peaks (Figure 2) can be indexed as the In$_2$O$_3$ cubic structure in the standard data (JCPDS: 06-0416). The cubic lattice parameter $a$ calculated from the XRD spectra are 1.0118(5), 1.0105(2), and 1.0096(4) Å for In$_2$O$_3$ samples calcined at 400, 500, and 600°C, respectively. These values are close to those of lattice constants $a = 0.32488$ nm and $c = 0.52066$ nm in the standard data (JCPDS: 06-0416). The crystallite sizes of the powders were estimated from X-ray line broadening using Scherrer’s equation [48] (i.e. $D = \frac{0.89\lambda}{(\beta\cos \theta)}$, where $\lambda$ is the wavelength of the X-ray radiation, $K$ is a constant taken as 0.89, $\theta$ is the diffraction angle, $\beta$ is the full width at half maximum (FWHM)), and were obtained to be 13 ± 1, 15 ± 4, and 15 ± 3 nm for In$_2$O$_3$ samples calcined at 400, 500, and 600°C, respectively. The particle sizes and lattice parameters of In$_2$O$_3$ samples are also summarized in Table 1.

### Table 1. Average particle sizes from XRD line broadening, cubic lattice parameter $a$ calculated from XRD spectra and the band gap ($E_g$) of the nanocrystalline In$_2$O$_3$ samples calcined in air at different temperatures for 2 h.

<table>
<thead>
<tr>
<th>In$_2$O$_3$ sample</th>
<th>Average particle size (nm)</th>
<th>Cubic lattice parameter $a$ (Å)</th>
<th>Estimated band gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcined at 400°C</td>
<td>13 ± 1</td>
<td>1.0118(5)</td>
<td>3.25</td>
</tr>
<tr>
<td>Calcined at 500°C</td>
<td>15 ± 4</td>
<td>1.0105(2)</td>
<td>3.31</td>
</tr>
<tr>
<td>Calcined at 600°C</td>
<td>15 ± 3</td>
<td>1.0096(4)</td>
<td>3.29</td>
</tr>
</tbody>
</table>

Fig. 1. TG-DTA curves of thermal decomposition of In$_2$O$_3$ precursor at a heating rate of 10°C/min in static air.
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The morphology and structure of the In$_2$O$_3$ samples were investigated by TEM. It is clear from the TEM bright-field images (Figure 3) that the morphology and size of In$_2$O$_3$ materials is affected by the calcination temperature. The TEM bright-field images of In$_2$O$_3$ (Fig. 3) show that the In$_2$O$_3$ sample calcined at 400 °C contains nanoparticles having sizes of ~5-10 nm whereas the In$_2$O$_3$ sample calcined at 500°C consists of well-dispersed particles of ~ 10-25 nm in diameter. The In$_2$O$_3$ sample calcined at 600 °C consists of larger particles with particle sizes in the ranges of 30-50 nm. The corresponding selected-area electron diffraction (SAED) patterns (Fig. 3) of all the In$_2$O$_3$ samples show spotty ring patterns without any additional diffraction spots and rings of second phases, revealing their crystalline cubic structure. Increase in calcination temperature results in stronger spotty pattern and the In$_2$O$_3$ samples calcined at 500, and 600 °C shows strong spotty patterns, indicating large particle size of highly crystalline cubic structure. Measured interplanar spacings ($d_{hkl}$) from selected-area electron diffraction patterns in Fig. 3 are in good agreement with the values in the standard data (JCPDS: 06-0416) as summarized in Table 2.

![Fig. 2. XRD patterns of nanocrystalline In$_2$O$_3$ samples calcined in air for 2 h at (a) 400 °C, (b) 500 °C, and (c) 600 °C.](image)

![Fig. 3. TEM images with corresponding selected area electron diffraction (SAED) patterns of the nanocrystalline In$_2$O$_3$ samples calcined in air for 2 h at (a) 400 °C, (b) 500 °C, and (c) 600 °C.](image)

**Table 2. Interplanar spacings ($d_{hkl}$) of In$_2$O$_3$ samples calculated from TEM selected-area electron diffraction patterns in Figure 3 compared with the reference values in the standard data (JCPDS: 06-0416).**

<table>
<thead>
<tr>
<th>Ring</th>
<th>Calculated interplanar spacing ($d_{hkl}$)</th>
<th>In$_2$O$_3$ sample (Å)</th>
<th>Standard data (JCPDS: 06-0416)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>In$_2$O$_3$ sample</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>calcined at 400°C</td>
<td>d$_{440}$ h k l</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.08128</td>
<td>3.13216 111</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.72131</td>
<td>2.75391 200</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.91022</td>
<td>1.93031 220</td>
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<td></td>
<td></td>
<td>1.67377</td>
<td>1.65155 311</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.57475</td>
<td>1.57095 222</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.36999</td>
<td>1.36613 400</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.24260</td>
<td>1.26204 331</td>
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<tr>
<td></td>
<td></td>
<td>-</td>
<td>-</td>
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<tr>
<td></td>
<td></td>
<td>1.10751</td>
<td>1.11244 420</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.04038</td>
<td>1.04829 511</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.96132</td>
<td>0.96307 440</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.90689</td>
<td>0.92393 531</td>
</tr>
</tbody>
</table>

Now let us consider the optical properties of the In$_2$O$_3$ samples. The UV-visible absorption spectra of all the In$_2$O$_3$ samples (Figure 4) exhibit a strong absorption below 450 nm (2.76 eV) with a well defined absorbance peak at around 288 nm (4.31 eV). The direct band gap energy ($E_g$) of the samples is determined by fitting the absorption data to the direct transition equation:

$$
\alpha h \nu = E_D (h \nu - E_g)^{1/2},
$$

where $\alpha$ is the optical absorption coefficient, $h \nu$ is the photon energy, $E_g$ is the direct band gap, and $E_D$ is a constant [49]. Plotting $(\alpha h \nu)^2$ as a function of photon energy, and extrapolating the linear portion of the curve to the absorption equal to zero as shown in the insets of Figure 4 gives the values of the direct band gap ($E_g$) to be 3.29 eV, 3.31 eV, and 3.25 eV for the In$_2$O$_3$ samples calcined at 400, 500, and 600°C, respectively. This value is lower than that of ~3.6 eV for the In$_2$O$_3$ reported in the literature [50].
known that the bulk In$_2$O$_3$ cannot emit light at room temperature. The spectra of all the samples also show a weak UV band having emission maximum at ~354 nm (3.51 eV). It is well known that the weaker UV emission observed on the samples calcined at 500 and 600°C compared to that of the sample calcined at 400°C may be due to their lower sensitizing centers. It is clearly seen from TEM results (Figure 3) that as the calcination temperature increases, the crystal size of In$_2$O$_3$ samples becomes larger. As a result, the number of sensitizing centers decreases owing to reductions in both the ratio surface area and concentration of oxygen vacancies, thus results in a decrease in PL intensity as observed in ZnO nanoparticles reported by Du et al. [55].

4. Conclusions

We have synthesized nanoparticles of In$_2$O$_3$ by a simple method using Aloe vera plant extract solution. Structural, morphological and optical properties of the synthesized nanoparticles were characterized. XRD and TEM analysis showed that the In$_2$O$_3$ samples are cubic with particle sizes of 5-50 nm. The morphology and size of In$_2$O$_3$ materials were affected by the calcination temperature. The prepared In$_2$O$_3$ nanoparticles showed a strong PL emission in the UV region. The strong emissions of In$_2$O$_3$ are attributed to the radioactive recombination of an electron occupying deep defect donors and cause the formation of new energy levels in the band gap of In$_2$O$_3$ samples. Thus, the PL emission from In$_2$O$_3$ nanoparticles results from the radioactive recombinations of an electron occupying oxygen vacancies with a photo-excited hole, which is analogous to the photoluminescence mechanism of ZnO and SnO$_2$ semiconductors [19,52,54]. It should be noted that the weaker UV emission observed on the samples calcined at 500 and 600°C compared to that of the sample calcined at 400°C may be due to their lower sensitizing centers. It is clearly seen from TEM results (Figure 3) that as the calcination temperature increases, the crystal size of In$_2$O$_3$ samples becomes larger. As a result, the number of sensitizing centers decreases owing to reductions in both the ratio surface area and concentration of oxygen vacancies, thus results in a decrease in PL intensity as observed in ZnO nanoparticles reported by Du et al. [55].

Acknowledgments

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