ORIGINAL ARTICLES

Effect of Stabilizer on the Physical Properties of Indium Tin Oxide Nanoparticles


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ABSTRACT

In this work indium tin oxide nanoparticles (ITO) have been synthesized by coprecipitation method with polyvinylpyrrolidone (PVP) as stabilizer. The effect of different molar ratios between PVP to indium and tin chloride on the particle size and crystallinity have been confirmed by X-ray diffraction (XRD) and transmission electron microscopy (TEM). X-Ray diffraction results showed that the crystallinity of ITO nanoparticles decreases and the particles size increases from 12 to 20 nm by increasing the ratios of PVP to metal chloride solution from (1:2) to (2:1). Infrared absorption spectra indicated the chemical coordination between In or Sn to oxygen atom of carbonyl group. The TEM results showed that the ITO nanoparticles were well dispersed and uniform in cubic shape. The calculated optical band gap of ITO nanoparticles decreases by increasing the ratios of PVP to metal chloride solution. D.C. Conduction mechanism have been discussed.

Key words: Co-precipitation, Indium tin oxide, Nanomaterials, Polyvinylpyrrolidone.

Introduction

Much effort has been made on the synthesis of ITO nanoparticles (Kim et al., 2004, Yu et al., 2002, Li et al., 2006, Ederth et al., 2005, Kim et al., 1999 and Herrero et al., 2002), especially on the preparation of ITO nanocomposites (Aegerter et al., 2003, Song et al., 2006, Solieman et al., 2006 and Leiber et al., 1998). It has been shown that the electrical, catalytic and optical properties of nanoparticles depend sensitively on its shape and size. Hence, shape-controlled synthesis of nanoparticles has been reported (Ahmadi et al., 1996, Pankove, 1971, Tauc et al., 1966, Ethayaraja et al., 2007 and Choo et al., 2006). Among these documents, solution-phase method seems to be of particular interest because of its simple operation. In the solution method for the synthesis of ITO nanoparticles (Kim et al., 2004, Yu et al., 2002, Li et al., 2006, Ederth et al., 2005, Kim et al., 1999 and Herrero et al., 2002), the particle size can be controlled by changing the precursor from indium nitrate and tin chloride to indium sulfate and tin-sulfate (Kim et al., 1999) and by controlling their growth rates (Herrero et al., 2002). However, as far as we could ascertain, little research has focused on the control of ITO nanoparticles' shape. Even though they obtained some cubic nanoparticles, they attribute the formation of cubic particles to the effect of pH value change (Kim et al., 2004 and Ahmadi et al., 1996), or the calcinations procedure (Kim et al., 2004).

In our present work, we prepared ITO nanoparticles with different shapes by controlling the ratios of polyvinylpyrrolidone (PVP) to metal chloride solution in the coprecipitation process.

2. Experimental:

2.1. Materials:

The main starting materials used were InCl₃·4H₂O(purity 99.2%), SnCl₄·5H₂O(purity 99.2%), Ammonia and PVP. All the materials were of analysis grades and used without further purification.

2.2. Synthesis and characterization of indium tin oxide nanoparticles:

30 grams of PVP were dissolved in 500 ml of de-ionized water and PH value was adjusted to 8.0 using diluted HCl solution at 80 °C. 3.77 grams of white (InCl₃·4H₂O) and 1.12 grams of white (SnCl₂·H₂O) were dissolved in 50 ml of de-ionized water. Several samples were synthesized by coprecipitation method with the same concentration and amount of metal chloride solution but different ratios of protective polymer material.
The ratios are \{(1:2), (1:1), (2:1)\}. After the addition of the protective polymer material (PVP) to metal chloride solution drop wise under stirring, during which aqueous ammonia was added to stabilize the PH 8.0 value in order to avoid the effect of PH change. The indium tin hydroxide suspension was isolated by centrifugation at 5000 rpm, washed with deionized water several times to remove chloride ions and dried at 100 °C. Then calcined at 800 °C.

2.3. Instruments:

The crystalline structure of the prepared samples was determined by X-ray Diffractometer Philips (PW 13900), using Cu Kα (λ = 1.54 Å). The vibrational spectra were collected using Jasco 6100 Fourier transform infrared (FTIR) Spectrometer. The samples were measured in mid-IR range using KBr method. The shape, morphologies and particle size distribution were studied using JEOL JEM 2010 transmission electron microscope operated at 200 kV accelerating voltage. The UV–visible spectra were measured in the range of 1000–2000nm using Jasco 570 UV–VIS-NIR spectrophotometer. The samples were prepared as suspensions using deionized water. D.C. conductivity have been measured, the samples were made in the form of disc of about 1.2 mm in thickness, under pressure 10 tons/cm². The two surfaces of each disc were coated with silver paint and checked for good conduction. The sample is inserted between the two cell electrodes. Calibrated furnace is used for heating the sample with constant rate. The temperature of the sample is measured using thermocouple connected to Digi-sense thermometer with junction in contact with the sample.

Results and Discussion

3.1 FTIR Spectra of ITO Nanoparticles Using PVP as Stabilizer:

The infrared spectra of the samples prepared at 80 °C, calcined at 800 °C for two different ratios ((1:2) and (2:1)) of PVP to metal chloride solution are seen in Figure (1: a–g). The absorption band appeared at about 3500 cm⁻¹ in Figure (1: a) of PVP assigned to the (OH) group of H₂O. The two noticeable absorption bands at 2956 and 2925 cm⁻¹ are corresponding to the symmetric and asymmetric stretching vibration of C–H bond in PVP. The strong absorption band at 1663 cm⁻¹ attributed to the stretching vibration of carbonyl group C=O. The absorption bands at 1291, 1319, 1374, 1425, 1440, 1463 and 1495 cm⁻¹ assigned to the vibration of heterocyclic in PVP. The bands at 1019, 845, 736 and 649 cm⁻¹ explained the C–N stretching vibration, out of plane C–H bending, rocking and OH wagging (Maoping Z. et al., 2000), respectively. By comparing the bands of PVP Fig.(1: a) with that ITOH/PVP Fig.(1: b–d) it can be noticed that, the absorption band appear at 1663 cm⁻¹ that assigned to C=O in PVP shift to lower wavenumber at 1631 cm⁻¹. This is may be due to the chemical coordination between In or Sn with oxygen atom through the lone pair of electron in C=O group. On the other hand the absorption band of C–N bond was shifted to higher wavenumber. This is because the polarity of C-N less than of C=O. From the spectra of ITOH/PVP nanocomposite Fig. (1: b–d) it was observed that, a new band appeared at 3435 cm⁻¹. The appearance of this band confirmed the formation of ITOH/PVP nanocomposite. The new bands appeared at 529, 444 and 412 cm⁻¹ may be due to the vibrations of (Sn-O and In-O). These bands shows in Figure (1: c, d) become more intense with increasing the metal chloride ratios. By comparing Figure (1: b–d) with Figure (1: e–g) to study the effect of calcinations process on ITOH/PVP nanocomposite it can be shown that, the bands (2956, 2925), (1663),( 1291, 1319, 1374, 1425, 1440, 1463 and 1495) and (1019) cm⁻¹ which assigned to (C-H), (C=O), (Heterocyclic) and (C-N) vibrations in PVP will disappeared because the destroying of polymer branch by calcined at 800 °C. The band 3435 cm⁻¹ decreased in Figure (1: e–g) due the transformation of ITOH/PVP nanocomposite to ITO nanoparticle. The absorption bands appeared at 412, 444, 529 cm⁻¹ due to (Sn-O and In-O) become more intense by increasing the ratio of metal chloride solution. The new absorption band appeared at 974 cm⁻¹ assigned to (In-O).

3.2 X-Ray Diffraction Pattern of ITOH/PVP Nanocomposite and ITO Nanoparticles:

X-Ray diffraction of the prepared samples at 80 °C, calcined at 800 °C for two different ratios ((1:2) and (2:1)) of PVP to metal chloride solution are shown in Figure (2). From Figure (2: a,b), it can be observed that, there are only three peaks (200) centered at 22.8° represented pure cubic In(OH)$_3$(JCPDS card no. 16-0161), (112) centered at 31.9° confirmed the formation of Sn$_3$O$_2$(OH)$_2$(JCPDS card no. 25-1303) and (440) centered at 51.13° indicates the formation of cubic ITO. The intensity of these peaks was decrease by increasing the concentration ratio of (PVP). i.e the crystalline of (ITO) decreased by increasing the PVP ratio. By comparing pattern of ITOH/PVP nanocomposite Figure (2: a, b) with pattern of ITO nanoparticles Figure (2: c, d) it can be noticed that, disappearing of two peaks (200) and (112) and a new three peaks appeared (222), (400) and (622) centered at 31.1°, 36.2° and 62° respectively due to the formation of cubic ITO nanoparticle. The low intense
peak (440) centered at 51.13°. Figure (2: a,b) of ITOH/PVP become more intense in Figure (2: c, d) of ITO due to complete thermal transformation process of ITOH/PVP nanocomposite into ITO nanoparticles.

Fig. 1a-g: The infrared spectrum of: (a) PVP, (b), (c) and (d) ITOH/PVP nanocomposite, prepared at ratios of PVP to metal chloride solution (1:2), (1:1) and (2:1), respectively, (e), (f) and (g) ITO nanoparticles after calcinations at 800 °C.

Fig. 2:a-c: X-Ray diffraction pattern of (a), (b) (ITOH/PVP) nanocomposite prepared with ratios of PVP to metal chloride solution (1:2) and (2:1), respectively and (c), (d) after calcinations at 800 °C.

3.3. Transmission electron microscope (TEM) data:

The TEM images of ITOH/PVP nanocomposite and ITO nanoparticles prepared at different molar ratios of PVP to indium and tin chloride are shown in Figures (3: a-f). From Figure (3: a-c) of ITOH/PVP nanocomposite
it can be noticed that, ITOH nanocomposites are formed in the branch of polymer and appeared as a dark core. The spherical shape and average particle sizes were estimated at 32.4, 35 nm at the ratios (1:2) and (1:1) of PVP to indium and tin chloride respectively. By increasing the ratio of PVP to (2:1) Figure (3: c) it is clear that, the most of formed particles in cubic phase with particles size 42 nm, this agreement with (Rongjun Pan et al., 2009). Figure (3: d-f) of ITO nanoparticles after cacinations at 800 °C showed that, the destroying of the polymer chain and decrease in particles size of nanoparticles with diameter of about 23.5, 28.8 and 30 nm of the ratios (1:2), (1:1) and (2:1) respectively.

3.4 UV-Visible Spectroscopic Results of ITOH/PVP Nanocomposite and ITO Nanoparticles:

Figure (4) shows the electronic spectra of PVP and ITOH/PVP nanocomposite. From this Figure (4: a) it is clear that, there is no absorption bands appear in the spectral range (200-1000 nm) of PVP polymer. The absorption band which appeared at shorter wavelength in Figure (4: b-d) indicate to the formation of ITOH nanoparticle in PVP through its branch polymer. The positions of the absorption band appeared at about 400 nm which characterized the exitonic band appear at nearly the same wavelength for different concentration of PVP. These results were confirmed by X-ray data. There is no absorption bands were appeared for all samples at high wavelength. Figure (5) shows the electronic spectra of ITO nanoparticles after calcinations at 800 °C. From this
Figure it is clear that the absorption edge has been appear at 340 nm. This may be due to the thermal transformation of ITOH/PVP nanocomposite into ITO nanoparticle.

![Figure 4](image1.png)

**Fig. 4:** a-c: UV-Vis spectra of ITOH/PVP nanocomposite prepared at different ratios of PVP to metal chloride solution (a) (1:2), (b) (1:1), (c) (2:1) respectivily.

![Figure 5](image2.png)

**Fig. 5:** a-c: UV-Vis spectra of ITO nanoparticle prepared at ratios of PVP to metal chloride solution (a) (1:2), (b) (1:1), (c) (2:1) respectivily, calcined at 800 °C.

The optical band gap ($E_g$) was determined from the experimental values of the absorption coefficient $\alpha$ as a function of the photon energy ($h\nu$) using the equation ($\alpha h\nu)^{2n} = C (h\nu-E_g)$ (Basu et al., 1997 and Usui et al., 2006), where $n = 1/2$ for direct band gap and $n = 2$ for indirect transition, $C$ is a constant depends on the electron-hole mobility. The absorption coefficient ($\alpha$) at corresponding wavelength was calculated from the relation $\alpha = \log(I/I_0) = \frac{1}{d}$, $d$ is the thickness and $A$ is the absorbance determined (Pankove, 1971). The values of the optical energy gab was determined by extrapolating the liner portion of the curves to ($\alpha h\nu)^2 = 0$ in Figure (6) and it were respectively equal 2.63, 2.27 and 2.09 eV of ratios (1:2), (1:1), and (2:1). The results indicated that the band gap were decreased with increasing the PVP ratios due to the increase in the particle size of ITOH/PVP nanocomposite. The value of optical energy gap of ITO nanoparticle shown in Figure (7) and equal 3.85, 3.5 and 2.75 eV of ITO nanoparticle prepared with ratios (1:2), (1:1) and (2:1) respectively, calcined at 800 °C.
3.5. D.C. Electrical Conductivity:

Electrical conductivity depends mainly on the mobility of charge carriers that can be correlated with the chemical composition and morphology of nanomaterial. Electrical conductivity of the ITO nanoparticles with different particle sizes and shapes is shown in Figure (8: a,b). It was observed that, the variation of log(\(\sigma\)) (\(\sigma\) in \(\text{cm}^{-1}\cdot\text{cm}^{-1}\)) with \(1000/(T)\) (K\(^{-1}\)) for nanocomposite samples follow the pattern of extrinsic semiconductor. It can be seen that, the general trend of the conductivity-temperature curves are similar; the curves passed through three main regions (I, II and III). The three factors dominating the variation of conductivity with temperature are (1) nature of trap distribution in the sample, (2) presence of impurities in the sample and (3) production of defects due to thermal excitation (Belsare N.G. and Deogaonkar V.S. (1998)).

The region (I) is identified with low temperature and extends upwards as far as the impurity exhaustion temperatures, \(T_s\). Thus, the region (I) is identified with the extrinsic conductivity of semiconductor due to the ionization of impurity atoms. The region (II) extends from the impurity exhaustion temperature \(T_s\) to the intrinsic temperature \(T_i\). In this region, all impurity atoms are ionized, but the intrinsic carrier are not yet excited to a marked degree because the density of carriers remains approximately constant and equal to the impurity concentration. Therefore, the temperature dependence of the conductivity of the semiconductors is decided by that of the carrier mobility. If the main scattering mechanism in this region is scattering by thermal vibrations of the lattice for which the mobility decreases with rising temperature, the conductivity will decreases within this region. On the other hand, if the main scattering mechanism is scattering by ionized impurities, the conductivity within region (II) will increase with rising temperature. The region (III) is identified with the transition to intrinsic conduction in semiconductor. Within this region, the density of carriers is equal to that of intrinsic carriers. The activation energies was calculated from Arrhenius relation \(\sigma = \sigma_0 \exp(-\Delta E/kT)\) at high and low temperature region \(E_{III}\) and \(E_I\) and tabulated in Table (1).
The variation of $\log(\sigma)$ with $1000/T$ (K$^{-1}$) for ITO nanoparticles prepared with different ratios of PVP to metal chloride solutions at (a) 1:2 and (b) 2:1, calcined at 800 °C

<table>
<thead>
<tr>
<th>Polymer ratio in ITO nanoparticles</th>
<th>Activation energy $E_{III}$ (eV)</th>
<th>$E_0$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:2</td>
<td>0.133</td>
<td>0.011</td>
</tr>
<tr>
<td>2:1</td>
<td>0.102</td>
<td>0.027</td>
</tr>
</tbody>
</table>

From Figure (9: a,b) we can observed that, the relation between $\log(\sigma T^{1/2})$ versus $(T^{-1/4})$ and indicated that the good fit for ITO samples. In this conduction mechanism, there is a strong evidence for phonon-assisted hopping conduction for the samples under investigation.
Fig. 9: a,b The relation between log(σT^{1/2}) versus (T^{-1/4}) for ITO nanoparticles prepared with different ratios of PVP to metal chloride solutions at (a) 1:2 and (b) 2:1, calcined at 800 °C

Conclusion:

ITO/PVP nanocomposites and ITO nanoparticles have been prepared by coprecipitation method. The shift to lower wavenumber of C=O absorption bands indicated to the chemical coordination between In or Sn with oxygen atom through the lone pair of electron on C=O group. The absorption bands appeared at (529, 444, 412 cm^{-1}) due to the vibrations of (Sn-O and In-O). X-ray indicates that the crysallinity of ITOH decreases by using PVP as stabilizer. The particle size increases by increasing the ratio of capping material. The optical band gap has been depend on the ratio between PVP and metal chloride. The D.C. electrical conductivity mechanism have been determined and discussed.

References