Synthesis and characterization of Sb doped SnO$_2$ for the photovoltaic applications: different route

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Keywords: dye sensitized solar cell, antimony doped tin oxide, hydrothermal

Abstract

Antimony doped tin oxide (ATO - Sn$_{0.92}$O$_2$:Sb$_{0.08}$) nanoparticles were synthesized by different chemical routes such as Hydrothermal (HT), Sol-gel (SG) and Sonochemical (SC) methods. The XRD pattern of the samples shows that Sb ion successfully incorporated into Sn lattice without altering the crystal structure. Optical spectral analysis of the samples indicates more absorption in the visible region. The vibrational modes of the ATO nanoparticles were characterized by FTIR spectra. DSSCs were fabricated with the as-prepared ATO nanoparticles from different routes, Eosin-Y dye, I$^-$/I$_3^-$ redox couple as electrolyte. I–V characteristics of the as fabricated devices were recorded to estimate the efficiency of the device. Our results indicate the DSSC fabricated using the hydrothermally synthesized ATO nanoparticle gives good efficiency ($\eta = 4.15\%$) comparing to the DSSCs fabricated using NPs synthesized via other methods. Hence, hydrothermally prepared material is to be considered as a suitable optical window material for DSSCs.

1. Introduction

Hectic research has been going on for the past two decades, to commercialize low cost silicon-free solar cells. A successful prototype of dye sensitized solar cell (DSSC) was demonstrated in the year 1991 with 7% efficiency [1]. Selection of materials plays a vital role in deciding the performance of the solar cell. To give better performance DSSC should have a strong sensitizing dye and good electrolyte to achieve higher open circuit voltage ($V_{OC}$). Further, the anode materials should have a very high surface area to enhance dye adsorption and ultrafast electron injection from the excited dye to the TCO in addition for an efficient transport of charge carriers with minimal recombination loss of electrons [2–7]. So far many researcher works with TiO$_2$ as photo anode, which could absorb only 6%–7% of the solar spectrum [8, 9]. An alternative, earth abundant and low cost material with an excellent optoelectrical property is needed to replace TiO$_2$. However, tin dioxide (SnO$_2$), an important n-type semiconductor with a wide band gap (E$_g$ = 3.8–4.3 eV), exhibits excellent optical, electrical and chemical properties and high thermal stability. SnO$_2$ and SnO$_2$-based materials, such as Sb-doped SnO$_2$, Mn-doped SnO$_2$, Zn$_2$SnO$_4$, Cd$_2$SnO$_4$ and so on, have been extensively studied due to their favorable optical and electrical properties [10, 11].

It has been observed that Sb-doped SnO$_2$ (ATO) exhibits good optical property, high electrical conductivity and good stability [12, 13] all important for a photovoltaic and optoelectronic applications [13, 14]. It is interesting to note that the chemical and physical properties of these materials largely depend on the sizes and shapes of particles. And these materials have been prepared by many techniques such as sol–gel [13–15], hydrothermal [16], solvothermal [17], sonochemical [18], combustion [19], and other methods. In this present work we have been synthesized the Sb:SnO$_2$ nanoparticles by sol-gel, sonochemical and hydrothermal method with Sb doping concentration of 8%, as the photo anode material for the solar cell application [20].
2. Materials and methods

The starting precursor tin II chloride (SnCl$_2$.2H$_2$O) and antimony trichloride (SbCl$_3$) were purchased from Merck, Germany.

2.1. Sol-gel method

The stoichiometric amounts of precursors were dissolved in 100 ml of absolute alcohol with continuous stirring with the temperature maintained at 70 °C. While stirring, the pH value of the solution maintained about 10–11 by drop wise adding of aqueous ammonia solution to gel formation. Then the gel was aged overnight and dried in air at 120 °C for 2 h. Subsequently, the gel was calcined at 500 °C for 2 h.

2.2. Sonochemical method

The starting precursors were dissolved in 50 ml of absolute ethanol separately and then mixed together and acetylacetone was added. After 20 min, stirring the homogeneous solution was formed. Then, the prepared homogeneous solution was sonicated for 60 min by immersing an ultrasonic horn. While, sonication the pH value of the solution maintained about 9–10 using aqueous ammonia solution. The pale-white precipitate was obtained and washed several times with double distilled water and dried at 120 °C for 2 h. Finally, as-prepared precipitate was calcined at 500 °C for 2 h.

2.3. Hydrothermal method

The precursors were dissolved in 50 ml of alcohol separately and mixed together with continuous stirring. Then the solution was transferred to the 100 ml Teflon lined autoclave which was then kept in the oven at 180 °C for 4 h. The synthesized sample was washed several times with double distilled water and ethanol. Subsequently, the sample dried in air at 120 °C for 2 h and calcined at 500 °C for 2 h.

2.4. Characterization techniques

The phase purity of the as-prepared ATO samples were identified using XPERT PRO X-Ray diffractometer in the 2θ ranging from 10°–80°. The UV–vis DRS reflection spectra for the as-synthesized ATO nanoparticles were recorded wavelength ranging from 250 nm to 700 nm using Ocean Optics spectrophotometer. The morphologies of the samples were observed by scanning electron microscopy (Carl-Zeiss EVO). FTIR spectra of ATO nanoparticles were recorded in the range of 4000–400 cm$^{-1}$ using SHIMADZU IR affinity spectrophotometer with KBr technique. The current density-voltage (J–V) calibrations were done using Keithley 2450 source measuring unit (SMU), with 100 mW cm$^{-2}$ (1sun) AM 1.5 G simulated sunlight produced by a solar simulator.

3. Results and discussion

3.1. Structural analysis

Figure 1 depicted the XRD pattern of the ATO samples were prepared via different synthesis methods. From the XRD pattern, the selected peak at 2θ values equal to 26.77°, 33.89°, 37.98°, 51.75°, 54.67°, 65.57° and 71.33° corresponding to the orientation along (1 10), (1 0 1), (2 0 0), (2 1 1), (2 2 0), (3 1 0) and (3 0 1) planes were observed. All the diffraction patterns were well matched with a tetragonal cassiterite structure with space group P42/mnm (JCPDS card no. 88–2348) and its lattice parameter a = 4.57092 Å and c = 3.14933 Å and the volume = 65.8 Å. The preferential orientation (1 10) plane was slightly shifted towards higher angle, it can be observed that the dopant did not alter the unit cell structure [21]. No peaks arising from other crystallized impurities could be detected, indicating that only Sb ions were incorporated into the lattice of SnO$_2$ crystal structure with good crystallinity.

3.2. UV–vis DRS Study

The diffuse reflectance spectra of ATO nanoparticles were recorded in 250–750 nm wavelength regions and it was shown in figure 2. It can be seen that as-synthesized ATO nanoparticles were having more absorption in the visible region. The optical band gap values of the materials were obtained from the following expressions using the Kubelka-Munk function as:

$$ F(R) = \frac{(1 - R)^2}{2R} $$

$$ [F(R)h\nu]^\frac{1}{2} = A(h\nu - E_g) $$

(1)

(2)
where $F(R)$ is the absorption coefficient from Kubelka-Munk function, $R$ is the reflectivity, $A$ is proportionality constant, $h\nu$ is the photon energy, $E_g$ is the band gap energy. The value of $n$ is $1/2$ for direct type transition and 2 for an indirect type transition. The optical band gap of the ATO NPs was estimated as 3.68 eV for HT, 3.71 eV for SG and 3.76 eV for SC. Among these values HT synthesized ATO nanoparticles show better absorption in the visible region than the other samples.

3.3. Surface morphology analysis
The SEM images of ATO samples were shown in figures 3(a)–(c). Compared to the synthesis methods, the aggregation of the nanoparticles varies considerably, and the shapes of the ATO particles are clear in the sample prepared as hydrothermal method.
3.4. FTIR analysis

Recorded Fourier Transform Infrared (FT-IR) spectra of the ATO samples were shown in figure 4. The strong peaks appeared around 617 cm$^{-1}$ in all the spectra were assigned to the stretching vibrations of Sb-O bonds.

Figure 3. Scanning electron microscope images for the synthesized NPs, (a) SC, (b) SG and (c) HT.

Figure 4. FTIR transmittance spectrum for the synthesized NPs.
The broad peak in all the spectra ascribes octahedral SnO$_6$ structure formation in the unit cell. It is indicated that, Sb ions were incorporated into the SnO$_6$ octahedral structure without altering the crystal structure as confirmed by XRD studies. A weak peak appeared around 1622 cm$^{-1}$ in all samples corresponds to the bending vibrations H$_2$O molecule [24, 25]. A weak broad peak appeared at 3371 cm$^{-1}$ due to the stretching vibration of the hydroxyl group [26] the sample prepared via hydrothermal method. It can be seen that, the strongest vibration peak depends on shifting of the preferential orientation (1 1 0) plane.

4. Current-voltage characteristics

The ATO nanoparticles were coated on to the conventional FTO conducting glass plate. Before the coating the plates were cleaned ultrasonically in isopropanol. ATO NPs were coated via doctor blade method as the anode with the active area of 0.64 cm$^2$ and dried at room temperature for 10 min subsequently heated at 500 °C for 30 min. Then the film was immersed into the Eosin Y dye for 24 h. Platinum (Pt) coated FTO plate was used as the counter electrode. Both photo anode and the counter electrodes were sandwiched and I$^-$/I$_3^-$ redox couple electrolyte was introduced for the DSSC calibration. The assembled DSSCs were undergone for the current density-voltage (J–V) calibrations using Keithley 2450 source measuring unit (SMU), while irradiating 100 mW cm$^{-2}$ (1 sun) with AM 1.5 G simulated sunlight produced by a solar simulator. Before the calibration the system is calibrated with a silicon reference cell. The current density-voltage (J–V) plot is shown in figure 5.

The fill factor (FF) and power conversion efficiency ($\eta$) of the solar cells were determined from following equations (3) and (4),

$$FF = \frac{J_{\text{max}} V_{\text{max}}}{V_{\text{OC}} I_{\text{SC}}}$$  \hspace{1cm} (3)

$$\eta = \frac{FF V_{\text{OC}} I_{\text{SC}}}{P_{\text{in}}}$$  \hspace{1cm} (4)

where $V_{\text{OC}}$—open circuit voltage, $I_{\text{SC}}$—short circuit current, $V_{\text{max}}$—Voltage maximum and $J_{\text{max}}$—current density maximum at power maximum. From the J–V plot, FF and PCE were calculated and tabulated in table 1. The power conversion efficiency was found to be 4.15% for HT, 3.52% for SG and 3.16% for SC. The cell assembled using the hydrothermally synthesized ATO NPs. [27, 28]
5. Conclusion

In this work, ATO nanoparticles were successfully synthesized through different chemical methods. As-prepared ATO nanoparticles show tetragonal rutile structure with good crystalline nature. Among the all methods, hydrothermally synthesized (HT) nanoparticles show good absorption in the entire visible region and the spherical shaped morphology. The DSSCs were fabricated with the structure of FTO/ATO + EY/1 /I$_3$ redox couple electrolyte/Pt_CE using as-prepared ATO nanoparticles. The results indicate that hydrothermally synthesized ATO nanoparticle shows good efficiency ($\eta = 4.15\%$) and to be consider as a suitable optical window materials for DSSCs.

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