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STRUCTURAL, OPTICAL AND PHOTOCONDUCTIVITY CHARACTERISTICS OF SnO_2-ZnS NANOCOMPOSITE SYNTHESIZED BY A HYDROTHERMAL METHOD

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ABSTRACT

SnO_2-ZnS nanocomposite was successfully synthesized by a hydrothermal method utilizing tin chloride dihydrate, sodium hydroxide, zinc sulphate heptahydrate and sodium sulphide as precursors. The as-synthesized SnO_2-ZnS nanocomposite was characterized by powder X-Ray diffraction for determining the crystalline structure and grain size, the optical properties of the product and band gap energy were studied by UV- visible absorption spectroscopy. Fourier Transform Infrared Spectroscopy (FTIR) was also studied. SEM revealed the surface morphology of the sample and the electrical properties were confirmed by dielectric and photoconductivity studies.

KEYWORDS: hydrothermal, nanocomposite, photoconductivity

INTRODUCTION

Nanomaterials have the structural features in between of those of atoms and the bulk materials. The interesting facts about nanocomposites are that it will exhibit unique properties of two or more composed nanoparticles. [1-2]. SnO_2 nanoparticles are n-type semiconductors which have a wide band gap. Show many promising applications including solid state gas sensors[3-6], conducting electrodes[7], dye-sensitized solar cells [8,9] and transistors.[10]. ZnS is a II-IV semiconducting material with a wide band gap of 3.7 eV, high index of refraction, high transmittance in the visible range [11], and large exciton binding energy (40meV) [12,13]. It has a extensive range of applications as optical gas sensors, solar cells, and photoconductors [14, 15]. The composite of SnO_2 - ZnS nanocomposite yields unique properties which can be applied in advanced techniques for making optoelectronic devices and gas sensors.

The nanocomposites were synthesized by the hydrothermal method. It is a simple and ecofriendly technique for synthesizing nanocomposites of SnO_2 - ZnS. [16]. The as-synthesized particles were characterized by powder X-Ray diffraction for determining the crystalline structure and grain size, the optical properties of the product and band gap energy were studied by UV-visible absorption spectroscopy. Fourier Transform Infrared Spectroscopy (FTIR) was carried out to study the functional groups in the sample. The morphology and the size of the synthesized nanocomposite SnO_2 - ZnS were analyzed using HR SEM

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MATERIALS AND METHODS

All the chemicals tin chloride dihydrate ($SnCl_2.H_2O$), sodium hydroxide (NaOH), were of analytical grade, were supplied by Merck and used as received without further purification.

Synthesis of SnO_2 and ZnS nanoparticles

The tin oxide and zinc sulphide nanoparticles were synthesized in aqueous solution in an air atmosphere. In the typical experiment, tin chloride dihydrate ($SnCl_2.H_2O$) is dissolved in distilled water under continuous stirring for few minutes. Sodium hydroxide (NaOH) pellets is added slowly, to the above solution. The mixed solution is allowed to stir for a few minutes. The solution is next filled in a Teflon flask and kept in an autoclave for hydrothermal treatment. The process is carried out in an oven at 180˚C for 6 hours. The resulting precipitate was collected by filtration and washed with absolute ethanol and distilled water in sequence several times. This sample was finally dried in a hot air oven for 2 h at 800ºC. Similarly, for ZnS synthesis, zinc sulphate heptahydrate

($ZnSO_4.7H_2O$) is dissolved in distilled water kept under the stirring process for a few minutes. Sodium sulphide (Na_2S) is added slowly, to the above solution. The mixed solution is allowed to stir for 30 minutes. Then, the solution is filled in a Teflon flask and kept in an autoclave for the hydrothermal treatment. The process is carried out in an oven at 220˚C for 12 hours. The resulting precipitate was collected by filtration and washed with absolute ethanol and distilled water several times inorder to remove the unreacted ions. The sample was dried in furnace at 60ºC for 12hours.

Synthesis of SnO_2 - ZnS Nanocomposites

Inorder to synthesize the SnO_2-ZnS nanocomposite, the as-synthesized SnO_2 nanoparticles and ZnS nanoparticles were used. Both the chemicals in the powder form were taken and mixed together by weight. The mixed SnO_2 and ZnS nanopowders were taken in an alumina crucible and heat treated in a furnace at 800˚C for 3hours. The annealed particles are removed and ground to a fine powder.

Instrumentation

The crystal structure analysis was performed using X-Ray Diffraction (XRD). For the XRD, the Siefert 3003T/T X-Ray diffractometer with CuKα (λ = 1.5406 Å) radiation in the 2θ range 20º - 70º was used to identify the structural phase composition. The surface morphology of the samples was observed using a FEI Quanta FEG 200 Scanning Electron Microscope equipped with an Energy Dispersive X-Ray Analyser (EDAX) detector. The photon absorption property of the samples in the UV-Visible range was recorded using the double beam Perkin Elmer (model Lambda 35) spectrophotometer in the range 190-1100 nm and their band gaps were calculated. Using the Fourier Transform Infrared Spectrometer [FTIR–Perkin Elmer model Spectrum RX 1], the spectrum was recorded in the range of 400-4000 cm^{-1}. The electrical properties of the samples were measured by the HIOKI 3532-50 LCR Hitester. The Photoconductivity of the composites was measured by the Keithley 6514 electrometer.

RESULTS AND DISCUSSION

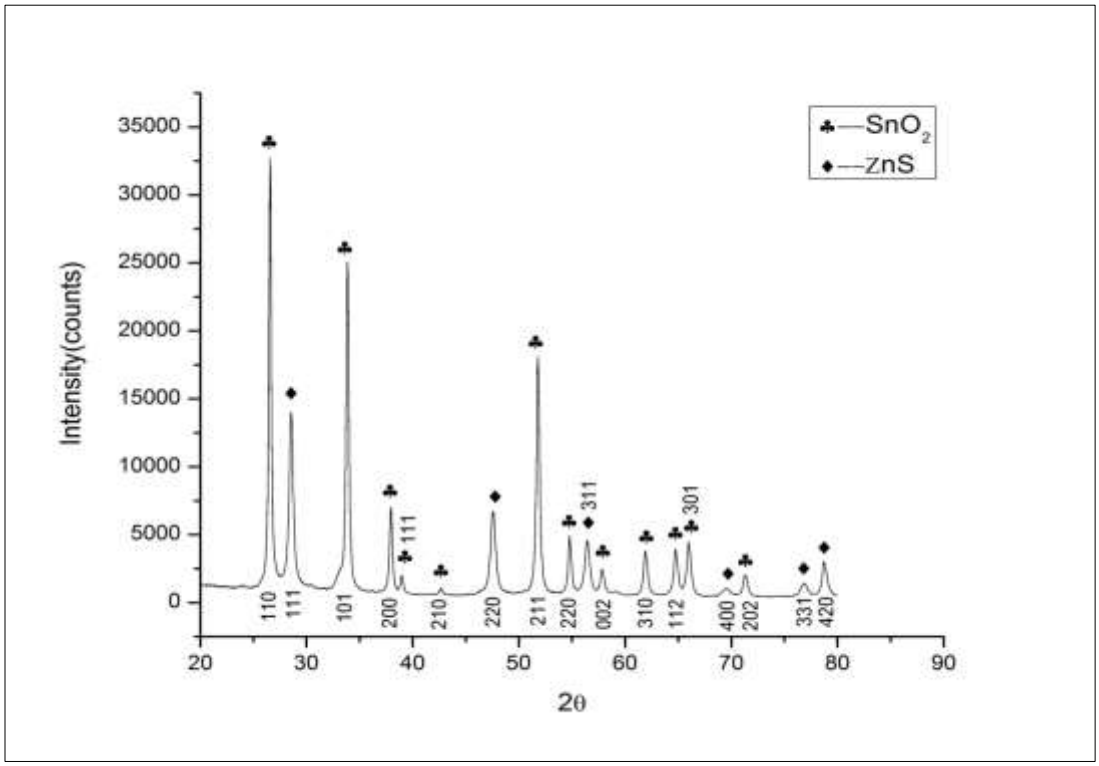

Figure 1: Typical XRD patterns of the as-synthesized ZnS-SnO_2 composite

The crystal structure and crystallinity of the as-prepared products were investigated by XRD. Figure 1 shows the XRD patterns of the as-prepared composite. All the diffraction peaks position and intensity agree very well with

their bulk counterparts standard diffraction pattern. The strong and sharp reflection peaks in the XRD pattern indicated that the composite products were well-crystallized. The pattern of the samples were indexed as a mixture of tetragonal SnO_2 (JCPDS No. 88-0287 with cell constants a=b=4.725 Aº and c= 3.186 Aº) and the cubic zinc blende ZnS (a = 5.401 Aº). No diffraction peaks from the other crystalline forms were detected. The average size of the nanocrystallites is calculated from full width at half maximum of XRD peaks using the Scherrer's formula.

$$d = \frac{k\lambda}{\beta \mathrm{Cos}\theta} \qquad (1)$$

From XRD data the average crystallite size of the SnO_2-ZnS composite were calculated to be 19.87nm using the Scherrer's formula.

Figure 2 shows the SEM images of the SnO_2-ZnS nanocrystals. The morphological analysis of the synthesized nanocomposite was done using HR SEM. Well-crystallized particles with estimated particle sizes of 18-22 nm were observed. The sample is composed of clusters of spherical nanoparticles with uniform size, shape and large specific surface area. This can significantly improve electron transfer rate which in turn contributes to the high photo catalytic activity. The captured image of the SnO_2-ZnS composite reveals clusters of spherical particles as its morphology.

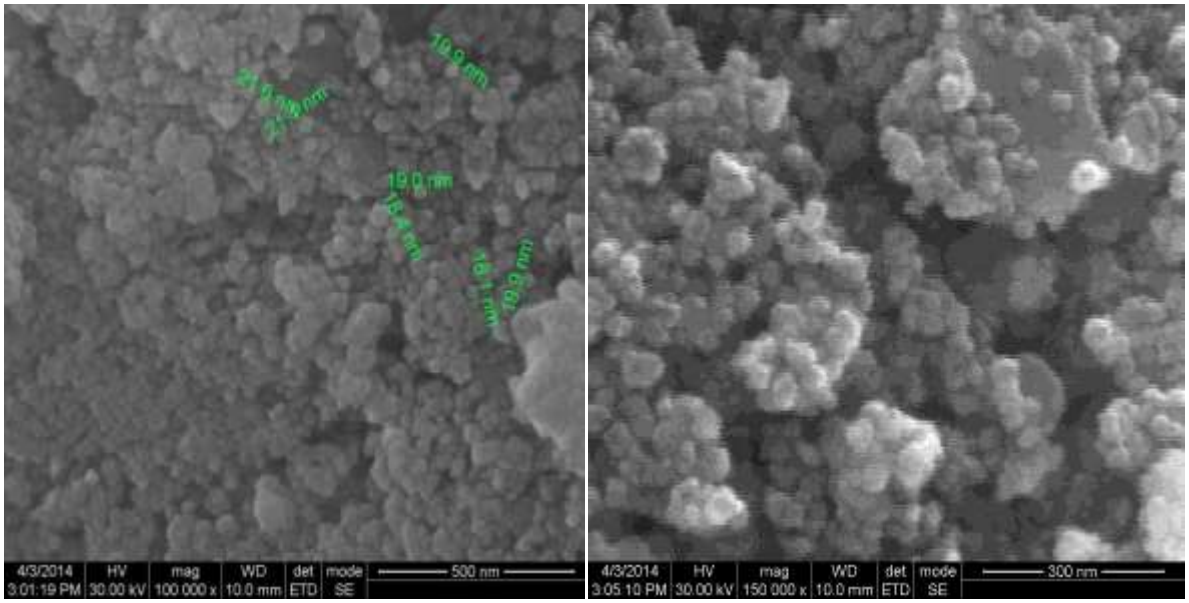

Figure 2: SEM images of SnO_2-ZnS nanocomposite structures obtained under hydrothermal conditions

Figure 3 presents the UV–Vis absorption spectra of the SnO_2-ZnS nanocomposites prepared. The data was recorded in the range 200-800 nm. The absorption spectra of the composite sample containing SnO_2-ZnS have been measured at room temperature. The absorption spectrum demonstrates an exited peak at 324.42 nm. The band gap of the bulk SnO_2 and ZnS is at 3.6 and 3.56eV respectively. The nanocomposite shows an obvious blue shift from 349 nm and 345 nm for bulk SnO_2 and ZnS, this can be attributed to the quantum size effects. The band gap of the composite thereby calculated using λ_{ex} was found to be 3.83eV which is larger than the band gaps of the two pure materials.

Figure 4 shows the FTIR spectrum of tin oxide - zinc sulfide composite taken between the ranges 400 – 4000cm^{-1}. 620.83cm^{-1} and 1116.1cm^{-1} peaks confirms characteristic ZnS vibration peaks. 1594.92cm^{-1} may be due to the microstructure formation of the sample. The broad absorption peak from 3000-3400cm^{-1} can be attributed to the OH group indicating the presence of water absorbed on the surface of the nanocrystals. An obvious shift of Sn-O vibration frequency may be due the formation of the composite. The bands at around 764.18 and574.24 cm^{-1} were attributed to Sn-O stretching modes of Sn-O-Sn and Sn-OH respectively [17].

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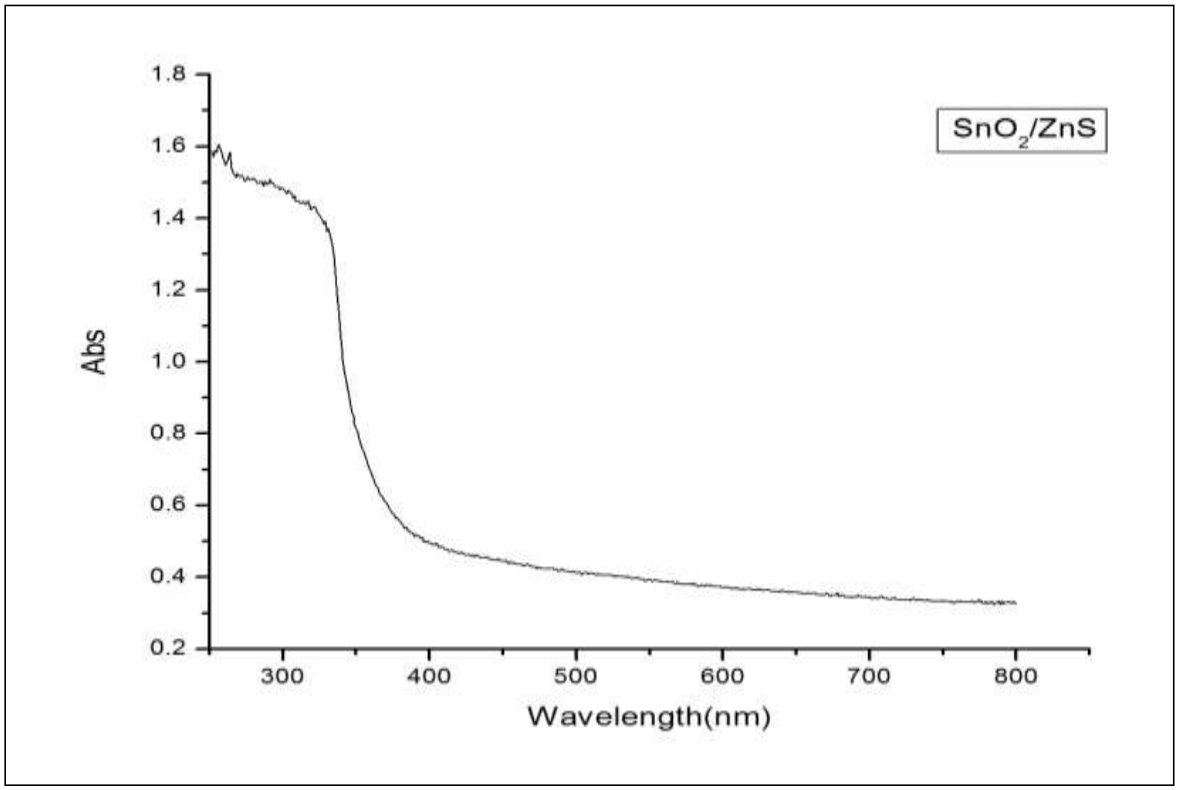

Figure 3: Absorbance spectra of SnO_2-ZnS nanocomposite

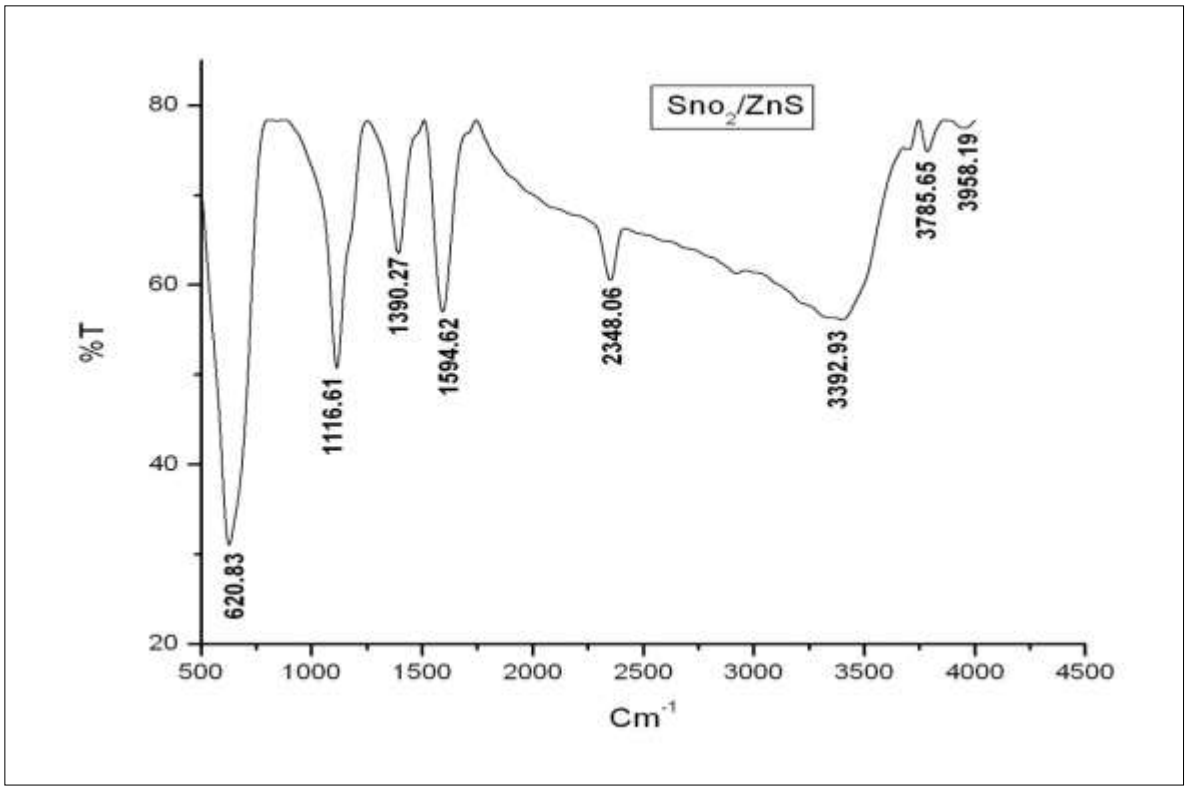

Figure 4: FTIR spectrum of the SnO_2-ZnS nanocomposite

Dielectric and Photo conductivity properties

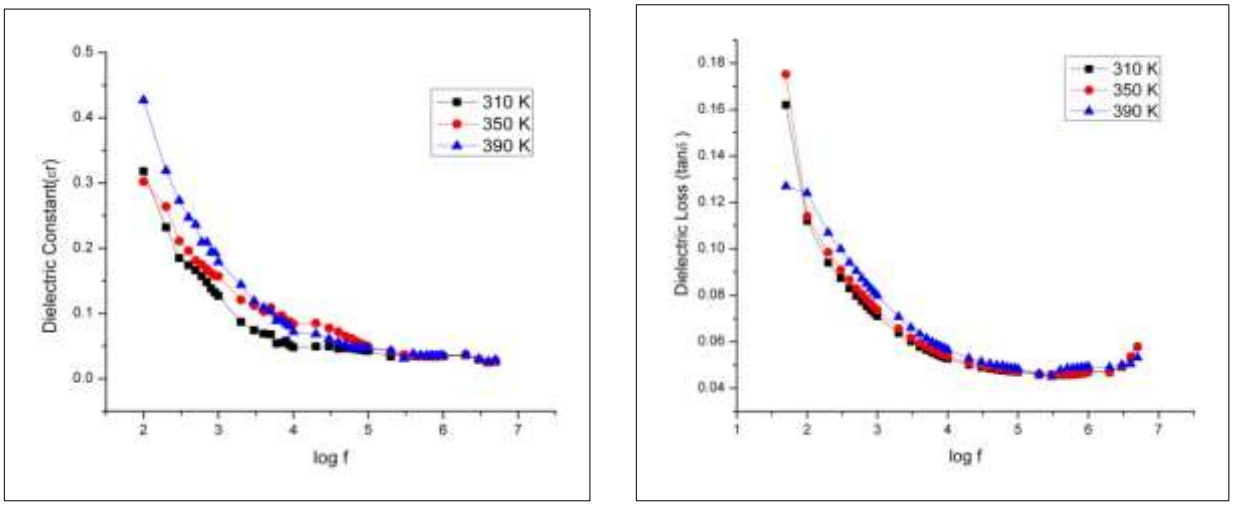

Figure 5: log f versus Dielectric Constant and Dielectric Loss for SnO_2-ZnS

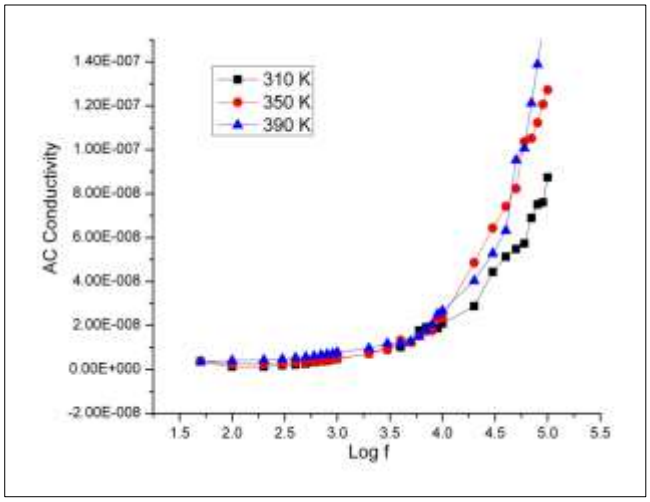

Figure 6: log f versus AC Conductivity for SnO_2-ZnS

The dielectric properties of the SnO_2 - ZnS composite was measured using the HIOKI 3532 LCR Hi TESTER in the frequency range from 50Hz to 5MHz. The pelletized sample was mounted between two electrodes. The capacitance of the parallel plate capacitor formed by the electrodes, with the sample as a dielectric medium was measured. The variation of capacitance was recorded in the frequency range at different temperatures.

The dielectric constant (ε_r) of the material was calculated for different frequencies from the measured capacitance values. The plots of the dielectric constant versus log f for the SnO_2-ZnS composite are shown in figure 5. It is observed that the dielectric constant has a high value in the low frequency region and thereafter decreases with the applied frequency.

The high value of (ε_r) at low frequencies may be due to the presence of all the four polarizations namely space charge, orientation and, electronic and ionic polarization and the low values at higher frequencies may be due to the loss of significance of these polarizations gradually. The variations of dielectric loss with frequency for SnO_2-ZnS composite are shown in figure 5. It is observed that the dielectric loss also has a high value in the low frequency region and thereafter decreases with the applied frequency

Fig 6 shows the variations of ac electrical conductivity with frequency for the SnO_2-ZnS composite. The ac conductivity was determined using the relation $\sigma_{ac} = \omega\ \varepsilon_o\varepsilon_r \tan\delta$ ($\omega = 2\pi f$, f is the frequency). With the high ac resistance, it can be mentioned that the space charge polarization plays an important role in the electrical property of the sample.

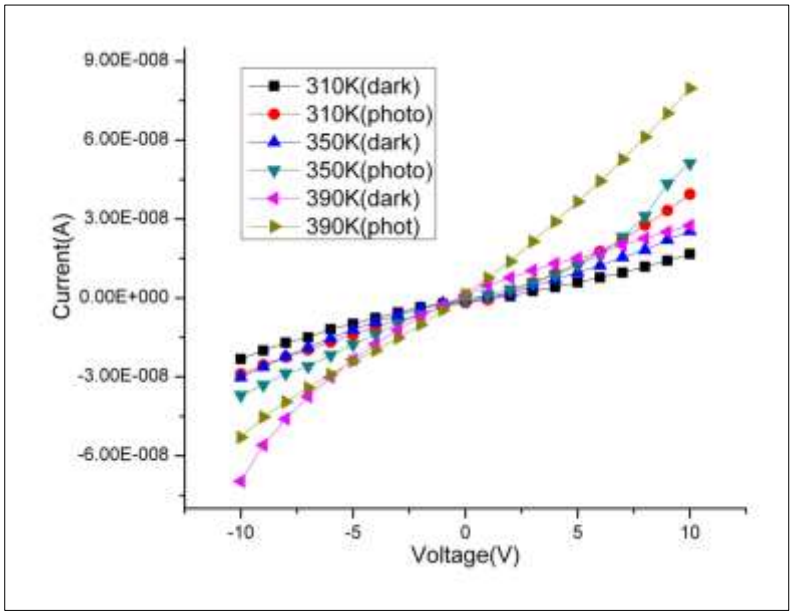

Figure 7: I–V characteristics of the SnO_2-ZnS nanocomposite

Fig. 7 shows the I–V characteristics of the SnO_2-ZnS nanocomposite The analysis was done in vacuum at room temperature, 350K and 390K, under a fixed level of halogen lamp (100W). The I–V curve measured in the absence of halogen lamp is also shown for comparison. It may be noted that both the curves exhibited non- ohmic characteristics showing the semiconducting behavior of ZnS and SnO_2 nanoparticles. It is observed from the plot that the dark current is less than photocurrent, suggesting that SnO_2-ZnS exhibits positive photoconductivity. This phenomenon can be attributed to generation of mobile charge carriers caused by absorption of photons. Such device has potential to be useful in designing ultra-fast optical sensors for portable photosensors and gas sensors applications.

CONCLUSION

In summary, SnO_2-ZnS nanocomposite have been synthesized via hydrothermal method. The structure, morphology, photoconductivity and optical properties of were investigated. The average grain size calculated by XRD analysis was found to be 24.02 nm. A morphology of clusters of spherical nanoparticles were be inferred from the HR SEM images of the SnO_2-ZnS composite. In addition, the HR SEM suggest that the mixing of SnO_2 and ZnS was not at the particle level but rather SnO_2 and ZnS formed clusters of like material. The optical absorption data demonstrated the bandgap widening of SnO_2-ZnS nanocomposite probably due to quantum confinement effects. In FTIR, it confirms the successful synthesis of SnO_2-ZnS nanocomposite due to the existence of peaks of both Sn-O bond and Zn-S bond. Through the dielectric analysis it was observed that the polarization effect contributes to the enhancement of dielectric response of the nanoparticles. The study of photoconductivity of SnO_2-ZnS nanocomposite with respect to voltage shows the variation in photocurrent and dark current. It is seen that SnO_2-ZnS exhibits positive photoconductivity, the phenomenon being attributed to the generation of mobile charge carriers caused by absorption of photons. The present work suggests very promising device applications of SnO_2-ZnS nanocomposite in optoelectronics devices, solar cells, photosensors and gas sensors.

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