Synthesis and dc conductivity study of polyvinyl alcohol-selenium nanofibers hybrid films

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Abstract

dc electrical properties of Selenium (Se) nanofibers impregnated polyvinyl alcohol films have been studied in the temperature (T) range of $298K \leq T \leq 350K$. The selenium nanofibers have been synthesized by the acidic decomposition of sodium selenosulfate. The dc conductivity of the films increases with increase in temperature and concentration of selenium nanofibers into the polyvinyl alcohol matrix. The activation energy for dc conduction decreases from 0.410 eV to 0.318 eV with increasing concentration of the nanofibers into the matrix.

1. Introduction

Polyvinyl alcohol (PVA)-based nanocomposite materials are of immense importance considering its potential applications in electronic industries [1-5]. PVA is a light-weight, flexible polymer with good film forming and electrical properties. Semiconducting nanostructures are also getting increasing interest from the research community as electronically important filler materials into the insulating polymer matrix. Among the different semiconductor materials, selenium (Se) nanostructures have several important properties like high photoconductivity, good thermoelectric and nonlinear optical properties. It can be used in application areas including electrical rectifiers and xerography [6]. Considering its wide extent of relevance and applicability, we have to pay much more attention to understand the intriguing properties of nanostructured selenium and its composites. Effective interaction of these nanostructures with polymer matrix can lead towards enhanced physical properties. Several synthesis routes have been reported in literature for the synthesis of selenium nanostructures [7-11]. Stroyuk *et al.* [7] has reported the structural and optical characterization of the selenium nanostructures synthesized from sodium selenosulfate. Shah *et al.* [8] has reported the synthesis of polyvinyl alcohol stabilized selenium nanoparticles. Schottky diode type behavior of selenium nanostructures have been reported by Chiquito *et al.* [12] and Sinha *et al.* [9] Photoconductivity of selenium nanotubes has been reported by Liu *et al.* [13]. In this work, selenium nanofibers have been synthesized in-situ in the chemical environment of PVA solution and then the dc electrical properties of the PVA-selenium nanofiber hybrid films have been investigated.

2. Experimental details

Polyvinyl alcohol (PVA) and selenium bulk powder were procured from LOBA Chemie. Oxalic acid dihydrate and sodium sulfite anhydrous were procured from Merck. In a typical synthesis procedure at first PVA stock solution is prepared by dissolving 6 gm PVA in 100 ml of double distilled water. The temperature was raised to 353 K along with continuous stirring to obtain a clear PVA stock solution. The sodium selenosulfate (Na_2SeSO_3) solution has been prepared by the method reported earlier [9]. Oxalic acid solution (0.31 M) was also prepared in 50 ml of water. In the next step, at first 19 ml of PVA solution was taken and 0.5 ml of Na_2SeSO_3 solution was added into it with continuous stirring. This is followed by the addition of 0.5 ml oxalic acid solution. The solution it turns reddish with the addition of oxalic acid which indicates the formation of nano selenium. It was then stirred continuously for 5 hours. The unreacted chemicals and salts were washed out following the method of Stroyuk *et al.* [7]. Finally, the solution was transferred onto a petridish and left for drying at room temperature for solvent evaporation. The resulting film was marked as S_1. Another sample was also prepared by taking 1.25 ml Na_2SeSO_3 solution with the appropriate amount of PVA and oxalic acid. The prepared sample was marked as S_2. A pristine PVA sample was also prepared and marked as S_0. The dried samples were cut into square pieces and left in a vacuum chamber until electrical measurements were performed. dc conductivity measurements of the samples (S_0, S_1 and S_2) were performed with a Keithley 6514 system electrometer connected with the sample holder. The temperature was varied (with the help of a programmable temperature controller) from room temperature to 350K.

3. Results and discussion

X-ray diffraction pattern (XRD) of the pure PVA and Se nanofiber impregnated PVA samples are displayed in figure 1. For pristine PVA films, sharp peak observed at around 19.6^0(2θ) due to the semi-crystalline nature of the polymer which results from the intermolecular hydrogen bonding mediated strong interaction of the PVA chains [4]. The other prominent peaks correspond to nanostructured selenium and are marked following ICSD code 22251
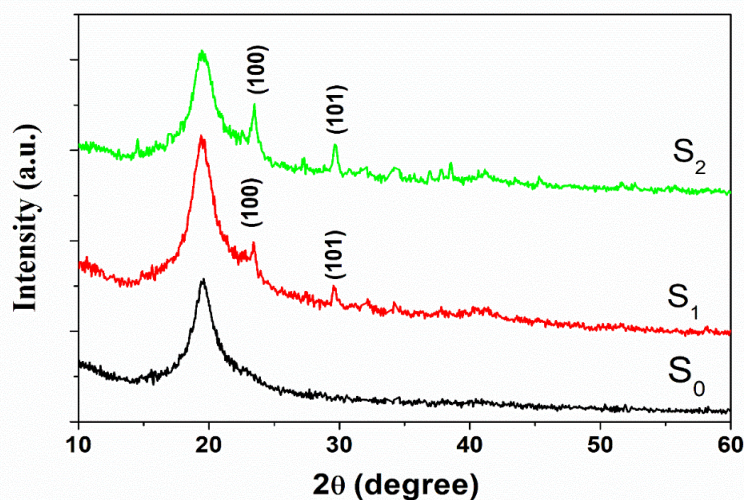

Figure 1: XRD pattern of the PVA films and PVA-Se nanofiber hybrid films

It has also been observed that the position of this peak is shifted slightly for the selenium nanofibre impregnated samples (hybrid films) as compared to the pristine PVA. Considering the position of the maximum of the halo the average inter-crystallite separation (R_{ics}) and d- spacing were calculated following the relations [14]-

$R_{ics} = \dfrac{5\lambda}{8\sin\theta}$ and $d_{spacing} = \dfrac{\lambda}{2\sin\theta}$, Where $\lambda = 1.54 \overset{0}{A}$ is the wavelength of the radiation used, θ is the Bragg's angle. The obtained d-spacing values and inter-crystallite separations are given in Table I.

Table I. *Intercrystallite separation of the Pristine PVA and Se nanofiber impregnated PVA films.*

Sample	2θ (degree)	$d_{spacing}$	I/I_0	R_{ics} ($\overset{0}{A}$)
S_0	19.58	4.528	100	5.660
S_1	19.42	4.565	100	5.707
S_2	19.40	4.570	100	5.713

So, the impregnation of selenium nanofibers within the PVA matrix increases the inter-crystallite separation. The high-resolution transmission electron microscopy image of the nanostructures displayed in figure 2. It was observed that the diameters of the nanofibers vary from 7.25 nm to 13.25 nm.
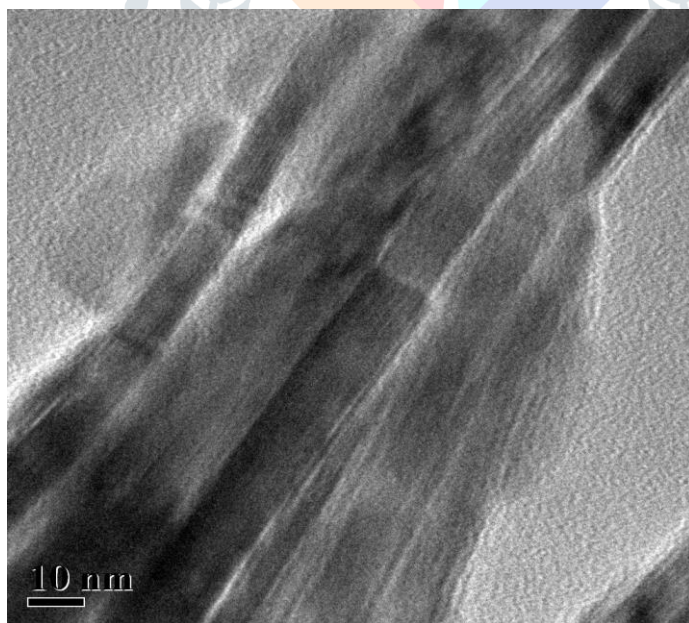

Figure 2: HRTEM image of the selenium nanofibers

The variation dc conductivity with temperature of the samples is presented in figure 3. It has been observed that the conductivity of the samples increases with increase in temperature and selenium nanofibers loading into the PVA matrix. The temperature dependency suggests a thermally activated process which can be expressed as-

$\sigma_{dc} = \sigma_0 \exp(-E_A / K_B T)$; Where σ_0 is the conductivity at the infinite temperature. E_A is the dc activation energy and K_B is the Boltzmann's constant.

Table II. *Extracted values of dc activation energies (E_A) for the samples*

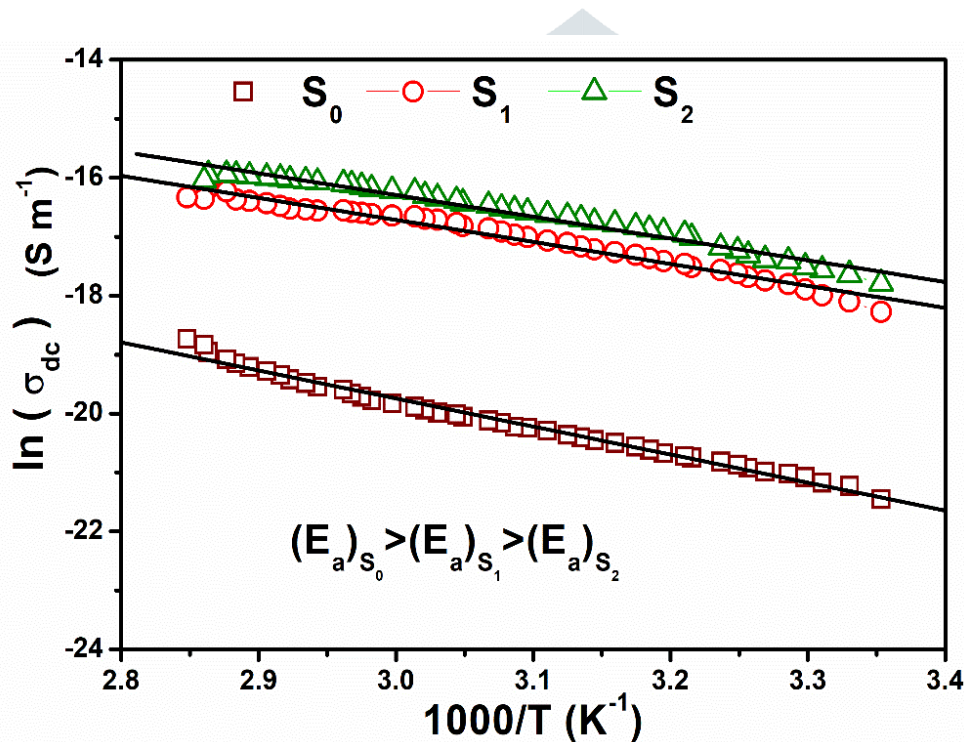| Sample	S_0	S_1	S_2
E_A (eV)	0.410	0.321	0.318

Figure 3: *Temperature variation of the dc conductivity (σ_{dc}) of the polyvinyl alcohol-selenium nanofiber hybrid films.*

The activation energies were calculated by linear fitting the $\ln \sigma_{dc}$ versus $1000/T$ graphs and are tabulated in Table II. From the extracted values of activation energies, we observe that with increase in selenium nanofibers concentration within the insulating PVA matrix the activation energy decreases. With increase in nanofibers concentration the mean inter-particle distances between the semiconducting islands decreases which in turn results in lowering the activation energies. The values of the activation energies also indicate that it is not the tunneling mechanism but rather hopping conduction mechanism of the charge carriers may be prevailing charge transport mechanism.

4. Conclusions

Polyvinyl alcohol-selenium nanofiber hybrid films have been synthesized by wet chemical synthesis process. It has been observed that with the impregnation of selenium nanofibers into the polymer matrix the d-spacing and intercrystallite separation increase as compared to pure polymer matrix. The dc conductivity of the hybrid films increases with increase in temperature and activation energy decreases with the increase in nanostructures concentration into the polymer matrix. However, detailed study is in process to understand the overall mechanisms clearly.

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