Synthesis, characterization and properties of Se nanowires intercalated polyaniline/Se nanocomposites

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Abstract. Present work reports novel synthesis of Polyaniline (PANI)/Se nanocomposites. Se nanowires are prepared from SeO₂ under assistance of vitamin C and polyaniline is synthesized through chemical oxidation. The effect of composition of Se nanowires on the properties of polyaniline was investigated and five orders increase in conductivity after doping has been observed. The electrical properties of nanocomposites show that conduction is through hopping process due to the wide range of localized states present near fermi level. FTIR (Fourier Transform Infrared spectroscopy) and ultraviolet (UV)-visible studies confirm the occurrence of polyaniline in conducting emeraldine salt form in the composites and suggest incorporation of Se in polymer. The optical studies indicate that absorption mechanism is due to indirect allowed transition and the optical band gap tends to decrease after doping. The thermal stability of composites has been ascertained on the basis of DSC (Differential Scanning Calorimetry) measurements. TEM (Transmission Electron Microscopy) and SEM (Scanning Electron Microscopy) analysis have also been carried out for morphological studies.

Keywords: polymer composites, DC conductivity, FTIR, UV-visible, thermal properties

1. Introduction

In recent years, with the rapid development of nanotechnology and composite materials, polyaniline (PANI) nanocomposites have attracted considerable interest. PANI is one of the most promising conducting polymers due to its high conductivity, easy preparation, good environmental stability and large variety of applications [1]. Unlike other conjugated polymers, PANI has a simple and reversible acid/base doping/dedoping chemistry, enabling control over properties such as solubility, electrical conductivity and optical activity [2].

Polymer nanocomposites show quite different properties from the constituent materials due to interfacial interactions between nanostructured semiconductors and polymers. Synthesis of PANI based

nanocomposites has led to a number of potential applications in electronic and optical devices, catalysis and analytical sensors etc. Some examples of these PANI nanocomposites are PANI/TiO₂, PANI/MnO₂, PANI/Ag, PANI/CdS, PANI/Poly(vinyl chloride) etc. [3–7]. However, studies on the interactions between PANI and chalcogenide nanoparticles are scarce. In our previous work, interactions of bulk Se with PANI have been reported [9]. To the best of our knowledge, Se nanowires containing polyaniline nanocomposites have not been reported elsewhere till now. Among chalcogenides Se nanoparticles have triggered great interest in researchers and therefore numbers of methods have been exploited for their synthesis and they have been widely used in electrical rectifiers, photocells, photographic

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exposure meters, xerography etc. [8]. We have employed a template free two step process to prepare Se nanowires. We believe that utilization of Se nanowires with polyaniline can result in a new material with useful properties. In this communication, we report synthesis, characterization and properties of PANI/Se nanocomposites.

2. Experimental

2.1. Materials

Aniline (Merck India, AR grade) refrigerated after distillation, Ammonium peroxodisulphate (APS) (Merck India, AR grade), Hydrochloric acid (Qualigens Fine Chemicals, LR grade), Ammonia solution in water (99%, Merck India), Chloroform (Merck India, Spectroscopic Grade), SeO_2 (Merck India, AR Grade) and β -cyclodextrin (Merck), Ascorbic acid (Sigma-Aldrich) and Ethanol (Merck) were used as such without further purification.

2.2. Synthesis and doping of polyaniline

PANI was synthesized through oxidative polymerization under assistance of APS [10]. APS was added to the acidified solution of aniline, followed by constant stirring for 12 hours at temperature between 0–5°C. A green colored powder, emeraldine salt (ES), was obtained which is the conducting form of polyaniline. This ES was then converted to insulating blue emeraldine base (EB) by treating with liquid ammonia and washed several times with distilled water and finally dried in the oven to a powdered form.

2.3. Synthesis of Se nanowires

Se nanowires were synthesized by using Ascorbic Acid as reducing agent for SeO_2 under the assistance of β -cyclodextrin followed by dispersion in ethanol in a room temperature synthesis method [11]. In this procedure, SeO_2 and β -cyclodextrin were dissolved in distilled water. The solution was promptly added to vitamin C (L-ascorbic acid) solution. After 4 h of reaction, product was collected by centrifugation followed by washing with distilled water. Gray colored Se nanowires of average diameter 60 ± 15 nm and upto several micrometers in length (see Figures 3 and 4) were obtained in this procedure. The chemical reaction may be represented by Equations (1) and (2):

2.4. Synthesis of nanocomposites

Finally dried emeraldine base was chemically doped with different concentrations of Se nanowires at room temperature. Se nanowires were ultrasonically dispersed in chloroform for 10 min at room temperature and added to swollen PANI (swollen by the effect of solvent). This solution was stirred for 24 h at room temperature in different ratios (80:20, 85:15, 90:10, 95:10, and 97.5:2.5 by weight). The doped PANI/Se nanocomposites were dried and grinded for making the samples. Samples were prepared in the form of pellets by using hydraulic press at a pressure of 767 kPa.

2.5. Characterization

Electrical conductivity of the pellets was measured in the temperature range of 300–450 K. The pellets were placed between two steel electrodes, fixed inside a metallic sample holder for conductivity measurements. A voltage of 1.5 V (through regulated DC supply) was applied to the pellet and resulting current was measured with a Keithley Electrometer model 6157A. The temperature measurements were done through a calibrated chromel alumel thermocouple mounted near the samples. Annealing of the samples was done before conductivity measurements at a vacuum of 10^{-3} Torr to avoid the effect of moisture absorption. Thermal analysis was carried out by Differential Scanning Calorimeter (Model-DSC plus, Rheometric Scientific Co. UK). The temperature precision of this equipment is $\pm 0.1^\circ\text{C}$. DSC scans were taken for undoped and Se nanowires doped PANI at $10^\circ\text{C}/\text{min}$ heating rates. The temperature range covered in DSC was from room temperature to 180°C . Undoped and doped nanocomposites were dissolved in chloroform to measure UV-visible absorption spectra using a Camspec M-550 double beam scanning UV-visible spectrophotometer. Scanning Electron Microscopy (SEM) was used to study the morphology of the sample using JEOL JSM 6380 SEM. Transmission Electron Microscopy (TEM) used to for the structural analysis of Se nanowires using FEI Tecnai G2 HRTEM at 200 kV. Samples for TEM were prepared by dropcasting a dispersion of Se nanowires onto a carbon coated copper grid. Fourier Transform Infrared (FTIR) spectra of

undoped and doped PANI/Se-KBr pellets were obtained by using Perkin Elmer FTIR spectrometer in the range from 400 to 4000 cm^{-1} at a resolution of 4 cm^{-1} .

3. Results and discussion

The DC conductivity of both undoped and doped composites is in good agreement with the Arrhenius relation [12], shown by Equation (3):

$$\sigma = \sigma_0 e^{(-\Delta E/k_b T)} \quad (3)$$

where ΔE is the activation energy, k_b is Boltzmann constant; T is temperature and σ_0 is the pre-exponential factor. The Arrhenius plots of conductivity of all the samples are shown in Figure 1. It is evident from this figure that conductivity increases exponentially with temperature. The DC conductivity of undoped PANI is found to be 1.27×10^{-8} S/cm. On doping with different levels of Se nanowires, conductivity increases from 10^{-8} to 10^{-3} S/cm attaining a maximum value in 10% (w/w) doped sample and then reducing in 20% (w/w) doped sample. If we compare these results with bulk Se doped PANI

Figure 1. Temperature dependence of DC conductivity in the temperature range (300–450) K for undoped PANI and PANI/Se nanocomposites with different concentrations of Se nanowires (w/w)

[9], we find a remarkable increase in σ and decrease in activation energy on addition of Se nanowires to PANI. This increase in conductivity after doping may be due to increase in the number of polarons formed during the doping process. The electrical conductivity of conducting polymers results from mobile charge carriers introduced into the electronic system through doping. At low doping levels these charge carriers are self-localized and form nonlinear configurations. Because of large interchain transfer integrals, the transport of charge is believed to be principally along the conjugated chains, with interchain hopping as a necessary condition [13, 14]. The nonlinear formation may be more in the case of heavy doping of 15% (w/w) doped composite, due to which it exhibits lesser conductivity than 10% (w/w) doped polymer and continues to decrease up to 20% (w/w) doped sample.

The Arrhenius plot of σ is a straight line, which indicates that conduction in samples is taking place via an activated process, having single activation energy in the temperature range 300–450 K. The values of σ_0 , ΔE and σ of the undoped and doped PANI samples have been calculated and are given in Table 1. It is clear from data that activation energy decreases after doping. The concentration dependent DC conductivity and activation energy values of all samples are shown in Figure 2. An increase in DC conductivity with corresponding decrease in activation energy is found to be associated with a shift of Fermi level in doped samples [15]. From a single value of activation energy, it is clear that the conduction is through the carrier concentration at the Fermi level. But the activation energy (ΔE) alone does not provide any information whether the conduction takes place in extended states or by hopping in localized states. This can be explained on the basis of the values of pre-exponential factor (σ_0). According to Mott and Davis [16, 17] value of σ_0 in the range 10^3 – 10^4 $\text{S}\cdot\text{cm}^{-1}$ indicates that the

Table 1. Electrical and optical parameters for PANI/Se nanocomposites doped with different concentrations of Se at temperature 350 K

S. No.	Samples	DC conductivity (σ_{dc}) [$\text{S}\cdot\text{cm}^{-1}$]	Activation energy (ΔE) [eV]	Pre-exponential factor (σ_0) [$\text{S}\cdot\text{cm}^{-1}$]	Optical band gap (E_g) [eV]	Extinction co-efficient (k) (at 550 nm)
1.	Undoped PANI	$1.27 \cdot 10^{-8}$	0.62	7.54	2.06	36.80
2.	2.5% doped PANI	$1.28 \cdot 10^{-3}$	0.13	$9.6 \cdot 10^{-2}$	1.77	13.73
3.	5% doped PANI	$1.87 \cdot 10^{-3}$	0.11	$7.06 \cdot 10^{-2}$	1.69	11.35
4.	10% doped PANI	$6.34 \cdot 10^{-3}$	0.12	$3.10 \cdot 10^{-1}$	1.59	32.18
5.	15% doped PANI	$4.50 \cdot 10^{-3}$	0.14	$9.80 \cdot 10^{-1}$	1.45	26.99
6.	20% doped PANI	$2.68 \cdot 10^{-3}$	0.16	$8.95 \cdot 10^{-1}$	1.56	31.36

Figure 2. Variation of DC conductivity ($\ln\sigma$) and activation energy (ΔE) versus undoped and doped PANI composites with different concentration of Se nanowires (w/w)

conduction takes place mostly in extended states. A smaller value of σ_0 indicates a wide range of localized states and the conduction is taking place by hopping process. In our case, the values of σ_0 are found to lie between the orders of 10^{-1} – 10^{-2} . Therefore, the conduction takes place by the hopping process due to wide range of localized states present in the sample. From the above results we may conclude that hopping mechanism is responsible for conduction in all of the nanocomposites. A smaller value of σ_0 also designates that the density of defect states increases in the sample and further supports our argument that the conduction mostly takes place by hopping process in all the composites.

Figures 3a, 3b show SEM and 3c, 3d show TEM images of Se nanowires. The nanowires are aesthetically dispersed in a uniform manner. These nanowires have an average diameter of 60 ± 15 nm with length upto several micrometers. Figure 4 shows the SEM micrograph of undoped PANI and PANI/Se nanocomposites in different compositions (w/w). These images depict that the doping of Se nanowires has a strong effect on PANI's morphology and with the increase of dopant contents, a transformation in morphology of PANI particles is observed. Figure 5 shows TEM image of 10% (w/w) doped PANI/Se nanocomposite which confirms encapsulation of Se nanowires by polymer. Figure 4a is typical SEM image of undoped PANI, when we compare it with the SEM images of composites, there we discover exfoliated dispersion of dopant in polymer giving rise to formation of intercalated nanocomposites (Figure 4b, 4c and 4d) and the size of polymer particles also increases upto the 10% (w/w)

doped sample favouring the increase in conductivity up to this level of composition. At higher concentration, the particle size does not increase appreciably (Figure 4e). The cluster size is found to reduce at 20% concentration of nanowires which is evident from (Figure 4f).

FTIR spectra of all the PANI/Se composites are shown in Figure 6. The five characteristic bands of PANI at 1580 cm^{-1} (assigned as C–C stretching of the quinoid rings), 1502 cm^{-1} (C–C stretching of benzenoid rings), 1300 cm^{-1} (C–N stretching mode), 1130 cm^{-1} (N–Q–N, where Q represents the quinoid ring) and 800 cm^{-1} (out-of-plane bending vibration of C–H on para-disubstituted rings) have been observed in the FTIR spectra of PANI/Se nanocomposites. This indicates that the spectrum of nanocomposites is identical to the emeraldine salt form of PANI [18]. Relative intensities of PANI bands decrease with decreasing PANI contents. Subsequently Se and Se containing organic compounds demonstrates absorption in far-infrared region only and do not exhibit specific absorption bands in the region between 400 and 4000 cm^{-1} of spectra. Se–Se stretching vibration shows absorption at 285 cm^{-1} . A new inherent peak at 830 cm^{-1} is observed in spectra of all of the nanocomposites. Pure PANI does not give absorption at this frequency. It is suggested that 830 cm^{-1} peak is an overtone of Se–Se stretching vibration, which has its main absorption peak at 285 cm^{-1} . Thorough information on PANI–Se interactions can be obtained by using spectrometric equipment which provides spectral data on far IR region (200 – 400 cm^{-1}) [19]. Proposed scheme of the formation of PANI/Se nanocomposites is shown in Figure 7.

The UV–visible absorption and reflection spectra are given in Figure 8. The $\pi \rightarrow \pi^*$ transitions of aromatic ring gives an absorbance peak at λ around 365 nm whereas inter-band $\pi \rightarrow \pi^*$ transition of excitation in the aromatic ring demonstrates a peak at 295 nm . Both the peaks show red shift of about 10 nm after doping with the increase in the dopant concentration. Red shift usually occurs due to the change in $\pi \rightarrow \pi^*$ transitions. The relation between optical band gap E_g , absorption coefficient α and the energy $h\nu$ of the incident photon is given by Equation (4) [20]:

$$ah\nu \propto (h\nu - E_g)^n \quad (4)$$

Figure 3. SEM images of PANI/Se nanocomposites with different contents of Se nanowires (a) 0, (b) 2.5, (c) 5, (d) 10, (e) 15 and (f) 20 wt%

The phonon absorption in many amorphous materials is found to obey the Tauc's relation (2). The index n has discrete values such as $1/2$, $3/2$, 2 or more depending on whether the transition is direct or indirect and allowed or forbidden, respectively. In the present case the photon energy is plotted against $ah\nu$, for $n = 2$ it gives a straight line fit, which implies that the samples obey indirect transi-

tion. From the absorption spectra the band gaps of all the samples are estimated by plotting energy ($h\nu$) versus $(ah\nu)^{1/2}$ (Figure 9). When compared to the undoped polymer, the optical band gaps of doped composites are found to decrease for all compositions. The decrease in band gap may occur due to the broadening of polaron bands, which is attributed to the increase in carrier concentration in

Figure 4. SEM micrographs of Se nanowires (a, b) and TEM of Se nanowires at different resolutions (c, d)

Figure 5. TEM of 10% (w/w) doped PANI/Se nanocomposite

the polymer after doping. The extinction coefficient (k) has been calculated using well known relation shown by Equation (5) [21]:

Figure 6. FTIR spectra of undoped and doped PANI at different Se nanowires concentrations (w/w)

$$k = \frac{\alpha \lambda}{4\pi} \quad (5)$$

where λ is the wavelength of the incident photon and α is the absorption coefficient. The optical parameters calculated from the UV-visible spectra are given in Table 1.

Figure 7. Schematic doping mechanism of PANI by Se

Figure 8. UV-visible absorption spectra of undoped PANI and PANI doped with different concentration of Se nanowires

Thermal properties of all the composites have been investigated by DSC study under non-isothermal conditions at heating rate of 10°C/min. Typical DSC curves for different samples are shown in Figure 10. The DSC traces of all the composites show single glass transition and single crystallization thus confirming the homogeneity of the material. Estimated values of glass transition temperature (T_g), crystallization temperature (T_c) and enthalpy change of the reaction (ΔH) are given in Table 2. It has been observed that T_g and T_c increase after doping. The increase in T_g may be explained on the basis of the fact that when dopant is added to polymer, it forms cross links between chains, owing to which the matrix become heavily cross linked and the steric-hindrance increases. This further makes the system more rigid and retards the tendency of crystallization. This rigid structure requires higher energy for softening and therefore T_g and T_c are observed at higher temperatures.

Figure 9. The photon energy ($h\nu$) versus $(ah\nu)^{1/2}$

Thermal stability of the samples has been ascertained through the $T_c - T_g$ difference. It is clear from Figure 11 that the value of $T_c - T_g$ increases up to 10% (w/w) doped composites; after this concentration a slight decrease is observed in $T_c - T_g$ values. Therefore, 10% (w/w) doped PANI/Se is the most stable composition among all other studied samples. In the non-isothermal study, the stability is usually investigated in terms of two independent factors. The first has already been discussed ($T_c - T_g$) and other is the heat content of the samples, i.e. enthalpy. The experimental evaluation of the crystallization enthalpy (ΔH_c) has been determined by measuring the area under the peak and converted into Joule through the use of instrument constant using the formula [22] (Equation (6)):

$$\Delta H_c = \frac{KA}{M} \quad (6)$$

where A is the area of crystallization peak, M is the mass of sample and K is the instrument constant which is found to be 1.2. It is observed that ΔH_c decreases with the increase in Se concentration because the samples being in the metastable state try to minimize its enthalpy as well as Gibbs free

Figure 10. DSC curves for all samples at heating rate 10°C/min (a) Undoped, (b) 2.5%, (c) 5%, (d) 10%, (e) 15%, (f) 20% Se nanowires doped PANI samples

Table 2. Thermal parameters of all samples at heating rate 10°C/min

S. No	Samples	T_c [°C]	T_g [°C]	ΔH_c [J/g]
1.	Undoped PANI	33±0.1	65±0.1	103.94±0.1
2.	2.5% doped PANI	46±0.1	101±0.1	85.63±0.1
3.	5% doped PANI	47±0.1	120±0.1	57.24±0.1
4.	10% doped PANI	43±0.1	124±0.1	28.76±0.1
5.	15% doped PANI	44±0.1	112±0.1	30.95±0.1
6.	20% doped PANI	45±0.1	123±0.1	30.38±0.1

energy at every temperature by elementary atomic motion to gain stability. The most stable composite will release the least energy to gain stability, as it already possesses a stable atomic configuration. Therefore, the most stable composite will have the least value of ΔH_c . In our case least value of ΔH_c corresponds to 10% (w/w) doped sample. Hence this composition (10% (w/w)) is most stable among all of the compositions of the series which is also confirmed from $T_c - T_g$ plots. The change in enthalpy and $T_c - T_g$ verses dopant concentration is shown in Figure 11.

Figure 11. Variation of $T_c - T_g$ and enthalpy change (ΔH_c) vs. PANI/Se nanocomposites in different compositions (w/w)

4. Conclusions

The semiconducting polyaniline and Se nanowires were successfully synthesized and PANI/Se nanocomposites were produced with different concentrations of Se. It has been observed that the conduc-

tivity increases by five orders of magnitude after doping. Conduction mechanism has been explained on the basis of pre-exponential factor range. SEM images show that dopant has been dispersed in polymer matrix and formation of clusters takes place supporting the variation in DC conductivity. The optical studies indicate that absorption mechanism is due to indirect allowed transition and optical band gap was found to decrease after doping. FTIR spectra corroborate the structural changes of PANI after doping of Se and confirm the presence of polyaniline in the form of conducting emeraldine salt. Stability of the composites has been explained on the basis of variation in $T_c - T_g$ and ΔH_c , which confirms that PANI/Se composites containing 10% Se (w/w) is most stable among all the nanocomposites. A similar trend in properties has also been observed in band gap measurements, SEM and DC conductivity measurements. Thus, we may conclude that Se nanowires doping has superior effect on properties of PANI in comparison to its bulk counterpart.

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