Semiconducting properties of nanofiber polyaniline organic semiconductor

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The electrical conductivity, optical and microstructure properties of the polyaniline nanofibers have been investigated. The SEM image of the polyaniline shows the formation of nanofibers with diameters of 30-50 nm and lengths of 300-1000 nm. The electrical conductivity results indicate that the polyaniline is an organic semiconductor. The room temperature electrical conductivity of the polyaniline nanofibers was found to be 5.67×10^{-4} S/cm. The electrical conductivity mechanism of the nanofibers polyaniline varies from the conduction by localized states to the conduction by extended states. In this nanofibers polymer, the current is carried by the movement of polarons partially delocalized on the polymeric structure. The optical band gap of the polymer was found to be 2.57eV of direct allowed transitions. The width of localized states for the polymer was found to be 0.30eV, which is from the conduction band edge to mobility edge.

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1. Introduction

The semiconductor polyanilines have attracted considerable attention in electronic devices due to their electrical and optical properties [1]. Polymeric molecules usually have dimensions ranging from 5 to 10 nm and are expected to exhibit size-dependent properties. The electronic and optical properties [2, 3] of these polymers in nanodimensions are found to be different from those of bulk polymers. Fundamental understanding of, how size and morphological changes influence the physico-chemical properties of polyaniline nanoparticles are of great technological interest [4]. PANI nanofibers were intensively investigated in the last 2 years and a variety of novel synthesizing methods and properties have been reported, which have been the subject of two recent reviews [5, 6].

The nanostructure may give new electrical and optical parameters such as electrical conductivity, refractive index, optical band gap. The main goals of this work include the analysis of the electrical, optical and microstructure properties and the fundamental understanding of the electrical and optical properties of nanofibers polyaniline.

2. Experimental

2.1. Synthesis of polyaniline nanofibers

Preparation of nanofibers polyaniline was described elsewhere [7]. All chemicals were of analytical grade from Xi'an Chemical Reagent Factory. Aniline was doubly distilled in the presence of zinc powder before use, and the others were used as received.

2.79g of aniline and 0.01g of iron (Ⅱ) chloride tetrahydrate ($FeCl_2 \cdot 4H_2O$) were dissolved in 300ml hydrochloric acid (1mol/L) and 75ml deionized water, respectively. The two solutions were mixed well in a beaker of 500 ml by placing the beaker in an ultrasonic cleaner (Model KQ-250DB, Kunshan Ultrasonic Instrument Company, Kunshan, China), which was operated at a power of 100W and a frequency of 40 kHz. The polymerization temperature was maintained at 25 ± 2^oC during the whole reaction stage. 68ml solution of hydrogen peroxide (H_2O_2, 6wt.%,) was added drop-wisely into the solution of aniline and $FeCl_2$ to initiate the polymerization. The addition of the oxidant solution was completed in about 50min. The ultrasonic irradiation was kept for 4h after completion of oxidant addition to ensure a higher conversion of the monomer. The green powder was separated from the reaction products by vacuum filtration and washed with hydrochloric solution until the filtrated became colorless. Then, the sample (filtrate cake) was collected and dried in vacuum (40^oC) for 20h. The hydrochloric acid doped PANI nanofibers (emeraldine salt, ES) were obtained. Dedoping of the polymer was performed by putting the sample in ammonia water (5wt.%) and stirring for 3h. After that, the sample was washed with distilled water until the filtrate become neutral and dried in vacuum (50^oC) for 20h. PANI nanofibers in emeraldine base (EB) were obtained.

2.2. Measurements

For studying the electrical conductivity measurements, the polyaniline nanofibers were pressed at 10 ton/cm^2 pressure forming a circular disc with diameter of 1 cm and thickness of 0.566 mm. Electrical conductivity was measured as a function of temperature by alternating polarity method to eliminate electrical polarization, triboelectric and piezoelectric effects using KEITHLEY 6517A electrometer. The reflectance spectrum of the polyanilines was recorded at ambient temperature using Shimadzu 3600 UV-vis-NIR spectrophotometer with integrating sphere attachment. The powder of the sample can be taken for morphology examination (JSM 6700F field emission scanning microscope, JEOL) directly without gold sputtering. The powder of the sample was dispersed in distilled water by ultrasonic irradiation to get dilute transparent dispersion of the PANI nanofibers.

3. Results and discussion

3.1 Microstructure properties of bulk and nanostructure polyanilines

The scanning electron microscopy (SEM) photograph of polyaniline nanofibers was shown in Fig. 1 [7]. It was shown that the diameters and lengths of those nanofibers were in the range of 30-50 nm and 300-1000 nm, respectively. As reported by Jing et al. [8], with ultrasonic irradiation introduced into the chemical oxidative polymerization of aniline, the secondary growth as well as the agglomeration of the polymerization products can be effectively suppressed, preserving the PANI with its intrinsic nanofibrillar morphology [9] in the final products instead of irregular aggregated PANI particles produced in the conventional synthesis.

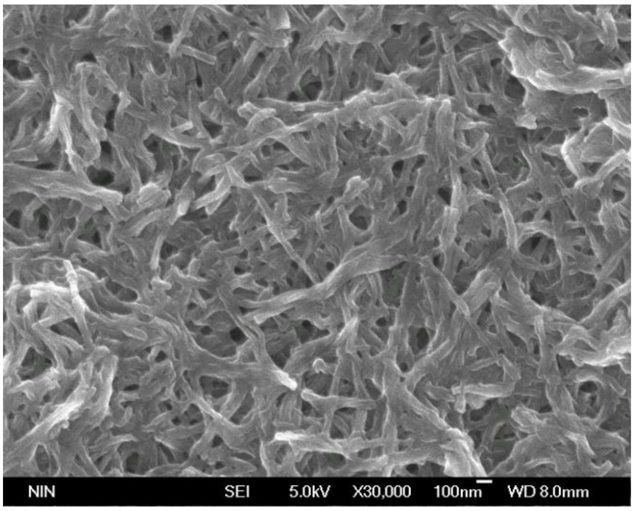

Fig. 1. SEM micrograph of the polyaniline nanofibers

3.2 Direct current conductivity properties of the polyaniline nanofibers

The temperature dependence of direct current conductivity of the polyaniline nanofibers is shown in Fig. 2. The electrical conductivity of the sample increases with increase of temperature. The conductivity dependence on temperature implies that the polyaniline nanofibers is an organic semiconductor. The conductivity curve indicates two linear regions, which are analyzed by the well-known relation,

$$\sigma = \sigma_o \exp(-E/kT) \quad (1)$$

where k is the Boltzmann constant, T is the temperature and σ_o is the pre-exponential factor. The activation energies of conductivity regions of the polyaniline nanofibers (E_I for region I and E_{II} for region II) were found to be 0.138 eV and 0.421 eV, respectively. The electrical conductivity of the polyaniline nanofibers at room temperature was found to be 5.67x10^{-4} S/cm. The room-temperature electrical conductivity of this as-formed sample was found to be in the range of 1.5-2.0 S/cm [7], after about 2.5 month, conductivity (5.67x10^{-4} S/cm) decreased significantly. This suggests that the polymer undergoes molecular changes over time. The electrical conductivity regions I and II correspond to different mechanisms. The first region corresponds to the hopping along intra-fiber conduction mechanism, while the second region corresponds to the hopping along fiber interconnects. The rate of conductivity in the second region is higher than that in the first region. In the second region, the increase rate of increase in conductivity is due to inter-fibers contact, because, as seen from SEM micrograph of the sample, the structure of the polymer is similar to network (Fig.1). This network facilitates the electron movement throughout the polymer via fiber inters connects and thus, the electrical conductivity increases strongly with temperature.

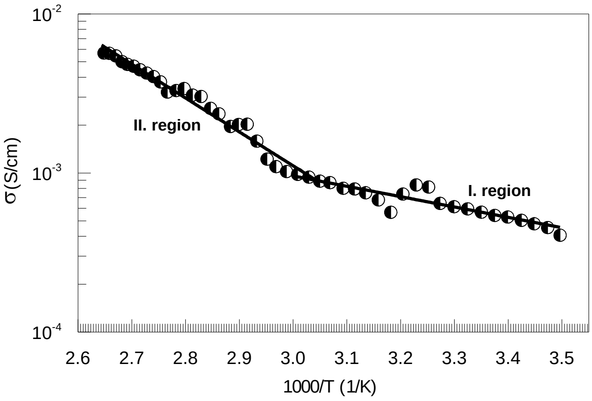

Fig. 2. Temperature dependence on electrical conductivity of the polyaniline nanofibers

X-ray diffraction results have shown that the polyaniline nanofibers have an amorphous structure [7]. In the amorphous materials, the electrical conductivity can take place via extended states and localized states. In order to check the existence of these mechanisms, we can use the pre-exponential factor values in Eq.1. Mott and Davis suggest that the pre-exponential factor σ_o for conduction in the extended states is of the order of 10^3-10^4 (S/cm), and a smaller value of σ_o indicates the conduction by hopping in the localized states [10]. The obtained σ_o ($8.56\text{x}10^{-2}$ S/cm) for region I is much smaller than 10^4 (S/cm); whereas, for the second region, the value of σ_o ($2.70\text{x}10^3$ S/cm) is of the order of 10^3 (S/cm). These obtained values suggest that in the first region, the conduction takes place via localized states, while in the second region, the conduction occurs by extended states. In this nanofibrillar polymer, the charge transport mechanism of the polaron is provided by the partially delocalization of polarons delocalized on the polymeric structure, because the polaron is formed in the nanofibrillar polymer when it was doped with hydrochloric acid. As seen in the UV-vis spectra of the polymer, the polaron band is formed in the red region of the UV-vis spectra [7].

The room temperature electrical conductivity value of the polyaniline nanofibers was compared with some polyanilines prepared by other methods. The electrical conductivity of the polyaniline nanofibers ($5.67\text{x}10^{-4}$ S/cm) is higher than that of the polyanilines by other method ($11.89\text{x}10^{-9}$ S/cm) [11] and ($0.47\text{x}10^{-7}$ S/cm) [12] and is of the same order of some polyanilines ($9.11\text{x}10^{-4}$ S/cm) [13], ($5.3\text{x}10^{-4}$ S/cm) [14], whereas its conductivity is lower than $7.5\text{x}10^{-2}$ S/cm [15]. This suggests that the effects such as chemical synthesis method, microstructure and doping degree are important parameters for the electrical conductivity of the polyanilines.

3.2. Optical properties of the nanofibers polyaniline

Fig. 3 shows the diffuse reflectance spectrum of the polyaniline nanofibers. The spectrum indicates an absorption band at 445.8 nm. This band corresponds to optical transition from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO), i.e., optical band gap transition. A minimum is observed in the reflectance spectra of the sample, which corresponds to the exciton formation. The optical band gap of the polymer can be obtained using the following relation [16],

$$F(R_\infty) = \frac{(1-R_\infty)^2}{2R_\infty} = \frac{k}{s} \qquad (2)$$

where R_∞ is the diffuse reflectance, k is the absorption coefficient and s is the scattering factor, respectively. The type optical transition for the polymer is determined using the well-known following relation

$$F(R_\infty) = B(h\nu - E_g)^m \qquad (3)$$

where *B* is an energy-independent constant and E_g is the optical band gap. In order to obtain the optical band gap of the polymer, we plotted $(h\square k/s)^2$ vs. h□□curve (Fig. 4). The optical band gap was determined by extrapolating the linear portion of the plot to $(h\nu k/s)^2 = 0$ (Fig. 4) and was found to be 2.57eV. This suggests that the fundamental absorption edge in the PANI polymer is formed by the direct allowed transitions. The optical band gap can be determined from derivate of diffuse reflectance, $\frac{dR}{dh\nu}$. For this, the plot of dR/dhν vs. hν was plotted, as shown in Fig. 5. The optical E_g value was determined from the maximum point of the peak and was found to be about 2.57eV. This value is in agreement with the above method. Furthermore, this result confirms the obtained E_g value from $(h\nu k/s)^2$ vs. hν curve. The optical band gap of the polyaniline nanofibers (E_g=2.57eV) is lower than that of the PANIs prepared by various methods (E_g=3.04eV) [17], (E_g=3.65eV) [18] and (E_g=2.79eV) [12]. The decrease in optical band gap of the polymer is due to the expanding of the localized levels when doped the polyaniline and in turn, the band gap is smaller.

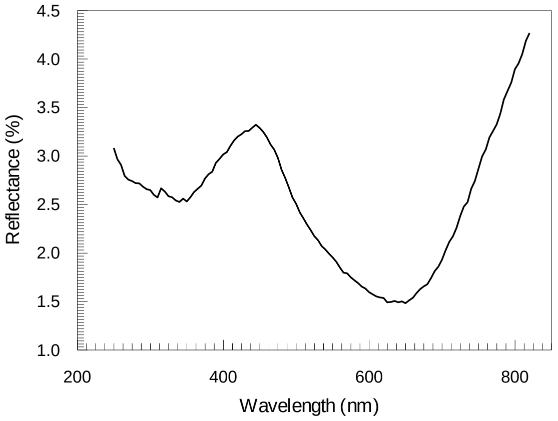

Fig. 3. Diffuse reflectance spectra of the polyaniline nanofibers

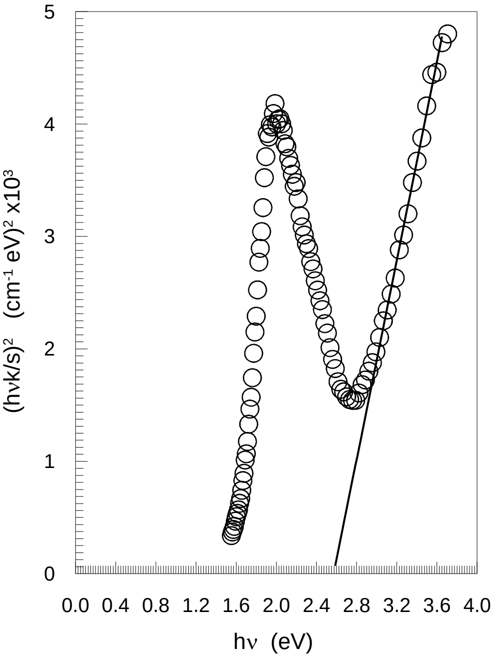

Fig. 4. Plot of $(h\nu k/s)^2$ vs. $h\nu$ of the polyaniline nanofibers

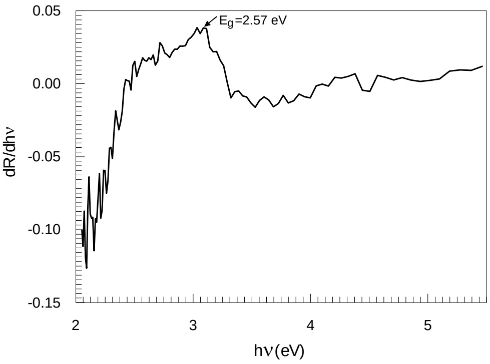

Fig. 5. Plot of dR/dhν vs. hν of the polyaniline nanofibers

The amorphous semiconductors have band tails, in which absorption coefficient depends exponentially on photon energy. The optical transition is from the valence-band tail states to the conduction band and from the extended states in the valence band to the conduction-band tail states. This transition can be analyzed using the equation,

$$F(R_\infty) = C\,exp(h\nu - E_g)/E_u \qquad (4)$$

where C is a constant, E_u is the band tail energy, i.e., Urbach energy [10]. The band tails is consisted due to structural disorder. In order to determine the band tail energy, we plotted the curve of the ln(k/s) vs. hν, as shown in Fig. 6. The E_u value was found to be 0.30 eV. This energy corresponds to the width of localized states, i.e., this width is from the conduction band edge to the mobility edge.

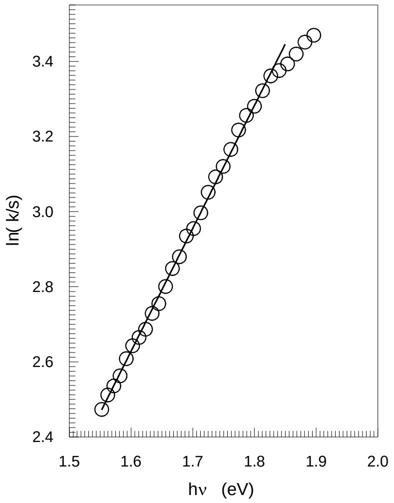

Fig. 6. Plot of ln(k/s) vs. hν of the polyaniline nanofibers

4. Conclusions

The electrical conductivity, optical and microstructure properties of the nanofibers polyaniline have been investigated. The SEM image shows polyaniline nanofibers with diameters and lengths in the range of 30-50 nm and 300-1000 nm, respectively. The electrical and optical results indicate that the polyaniline is an organic semiconductor with room temperature electrical conductivity of 5.67×10^{-4} S/cm and optical band gap of 2.57eV.

Acknowledgments

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References

[1] F. Yakuphanoglu, R. Mehrotra, A. Gupta, Manuel Munoz, Journal of Applied Polymer Science, Article in Press (2009).
[2] M. S. Cho, S. Y. Park, J. Y. Hwang, H. J. Choi, Mater. Sci. Eng. C. **24**, 15 (2004).
[3] T. M. Wu, Y. W. Lin, C. S. Liao, Carbon, **43**, 734 (2005).
[4] S. Goel, A. Gupta, K. P. Singh, R. Mehrotra, H. C. Kandpal, Mater. Sci. Eng. A, **443**, 71 (2007).
[5] J. X. Huang, Pure Appl. Chem. **78**, 15 (2006).
[6] D. H. Zhang, Y. Y. Wang, Mater. Sci. Eng. B **134**, 9 (2006).
[7] Y. Y. Wang, X. L. Jing, J. H. Kong, Synthetic Met. **157**, 269 (2007).
[8] X. L. Jing, Y. Y. Wang, D. Wu, L. She, Y. Guo. J. Polym. Sci. Part A: Polym. Chem. **44**, 1014 (2006).
[9] J. X. Huang, R. B. Kaner, Chem. Commun. **6**, 367 (2006).
[10] N. F. Mott; E. A. Davis, Electronic Processes in Non-crystalline Materials, Clarendon Press, Oxford (1971).
[11] S. Ameen, V. Ali, M. Zulfequar, Haq M. Mazharul, M. Husain, Current Applied Physics, **7**, 215 (2007).
[12] F. Yakuphanoglu, B. Filiz Şenkal, A. Saraç, Journal of Electronic Materials, online first (20008) (www.springer.com).
[13] H. Yan, N. Sada, T. Toshima, Journal of Thermal Analysis and Calorimetry, **69**, 881 (2002).
[14] H. Devendrappa, U. V. Subba Rao, M. V. N. Ambika Prasad, Journal of Power Sources, **155**, 368 (2006)..
[15] S. Palaniappan, Polym. Adv. Technol, **13**, 54 (2002).
[16] S. I. Boldish, W. B. White, Am. Mineral. **83**, 865 (1998).
[17] T. Welton; Chem Rev, **99**, 2071 (1999) .
[18] K. Sekigucki, S. Atobe, T. Fuchigami, Journal of Electroanalytical Chemistry, **557**, 1 (2003).

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