RESEARCH ARTICLE OPEN ACCESS

Study of the optical properties of Zinc doped Polypyrrole

Bishwajit S. Chakrabarty
Applied Physics Department, The M. S. University of Baroda, Vadodara.

Abstract
Polypyrrole is a well known conducting polymer whose electrical properties have been studied deeply. Amongst the various ways of polymerizing Pyrrole, chemical route was chosen for the present study. Ferric chloride was chosen as an oxidizing agent. Zinc was found to be an appropriate dopant. Zinc belongs to group IIB with atomic number 30 having electronic configuration [Ar] 3d10 4s2. An expected substitution of Zn with Nitrogen of Pyrrole would leave a single electron with Zn after bond formation, creating a probability of polaron and bipolaron band formations. Characteristic peak around 450nm is observed in all the samples confirming the formation of polypyrrole. Band gap of samples are found in semiconducting range. Apart from this, some of the important optical constants such as absorption coefficient, extinction coefficient, refractive index and optical conductivity have also been evaluated for all the samples and have been studied as a function of energy. The work presents the optical properties of this conducting polymer for making it a suitable candidate for optoelectronic devises.
Keywords: Chemical Oxidative polymerization, Optical conductivity, Absorption Coefficient, Extinction Coefficient, Refractive Index.

I. Introduction

Polyacetylene has been discovered in 1977 and was found to have conducting nature [1]. Extensive research on several conjugated polymers including poly(p-phenylene), polyaniline (PANI), polypyrrole, polythiophene, polyindole, polycarbazole, polyfluorene, poly(p-phenylenevinylene) and their substituted derivatives have led to their applications in rechargeable batteries, microelectronics, sensors, electrochromic displays, and light-emitting and photovoltaic devices [2,3].Conducting polymers like polypyrrole [4], polythiophene [5], or PEDOT [6,7], are well known as active materials for polymer electronics. In this present study we have carried out the chemical oxidative polymerization of Pyrrole. Element Zinc has the configuration of [Ar] 3d10 4s2. An expected substitution of Zn with Nitrogen of Pyrrole would leave a single electron with Zn after bond formation. Thus, creating a probability of polaron and bipolaron band formations.

II. Experimental

Pyrrole monomer was purchased from sigma Aldrich and was used as received. Analytical grade Ferric chloride and cadmium nitrate were purchased from qyalingens and were used as received. 1.42 grams of $FeCl_3$ was dissolved in 50ml 1M HCl at 5 ^oC under nitrogen atmosphere for 30 mins. After 30 mins 1.22 ml Pyrrole monomer was added to the mixture in a single step. The colour of the mixture immediately changed from pale yellow to dark green to black. The reaction was allowed to carry out for 30 mins. After 30 mins the black precipitates were filtered and were first washed with methanol and then with acetone. For the doping of Zinc, Zinc nitrate in different molar ratios was added to Pyrrole monomer and ultrasonicated for 15 mins. Zinc was doped in molar ratios of 5%, 10%, 15%, 20% and 25%.

III. Results and Discussions

UV-Vis Spectroscopy

The optical absorption spectra of the polymer samples were recorded in the range of 200 nm to 900 nm on the Thermo fisher equipment (figure 1). A major peak at 472 nm (2.62ev) was observed for undoped polypyrrole which is attributed to ∏-∏* inter band transitions and is and characteristic peak of conducting polypyrrole. Shoulder at 223 nm (5.55 ev) is also observed. This tiny shoulder is shifted to 302 nm (4.10 ev), 298 nm (4.16 ev), 244 nm (5.08 ev) and 281 nm (4.81 ev) when the material is doped with 5%, 15%, 20% and 25% Zn respectively. Although this peak vanishes when polymer is doped with 10% Zinc. Small humps around 850 nm indicating polaron bipolaron transitions for all the samples. A shift in characteristic wavelength is observed after doping. These observed shifts are due to dopant-polymer interaction. The spectra of doped samples show continuous absorption after 500nm indicating formation of polaron bipolaron bands. This rise observed after 500 nm up till 900nm can be called the broad free carrier band. The absorption shoulders for the samples in the range of 210 nm to 300 nm are attributed to the transition of electron from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) which is related to ∏-∏* electronic transition . Thereafter up till 496 nm the absorption peaks indicate the polaron transitions. The peak around 850 nm in

polypyrrole spectrum has been assigned to –NH– species, which are generated during doping.

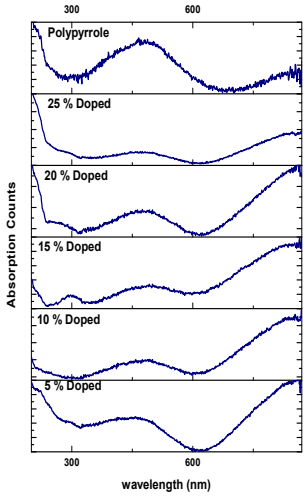

Figure 1: UV-Vis Spectra.

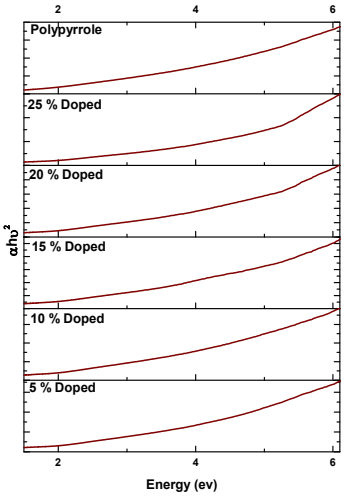

Figure 2: Tauc's Plot.

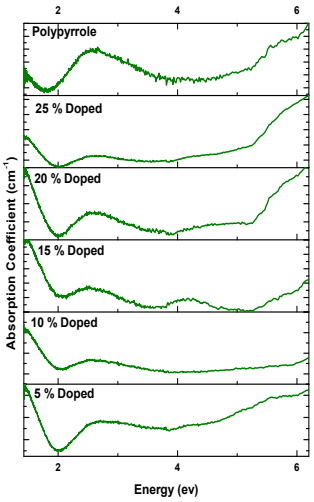

Figure 3: Variation in absorption coefficient with energy.

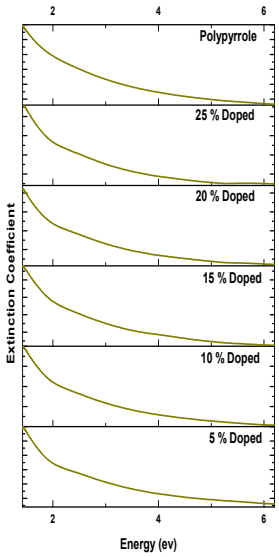

Figure 4: Variation in extinction Coefficient with energy.

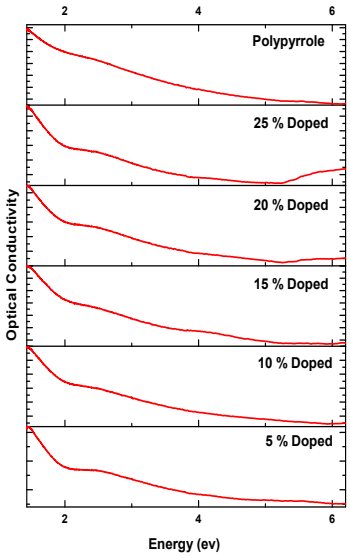

Figure 5: Variation in Optical Conductivity with energy.

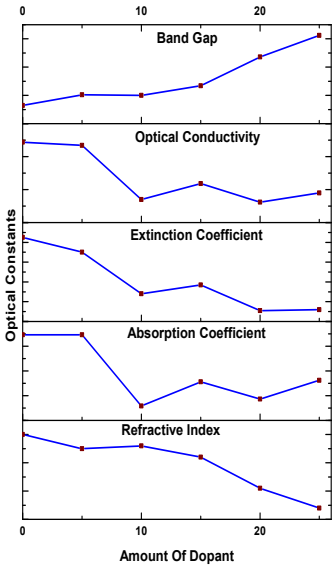

Figure 6: Variation in Values of Optical Constants with Amount of Zinc.

Table 1: Optical constants of all the samples

Amount of Zn	*Refractive index*	*Absorption coefficient*	*Extinction coefficient ($x10^{-5}$)*	*Optical conductivity ($x10^{10}$)*	*Band Gap (ev)*
0%	*2.4093*	*4.739574*	*1.65*	*2.72*	*2.82*
5%	*2.3586*	*4.739574*	*1.5*	*2.67*	*3.01*
10%	*2.3623*	*3.290987*	*1.08*	*1.85*	*3.00*
15%	*2.321*	*3.781526*	*1.17*	*2.09*	*3.17*
20%	*2.2103*	*3.433773*	*0.91*	*1.81*	*3.68*
25%	*2.1424*	*3.816071*	*0.92*	*1.95*	*4.06*

The energy band gap of the polymers has been calculated with the help of absorption spectra. To calculate the optical band gap energy from absorption Spectra, the Tauc's relation is used.

$$\alpha h\nu = A [h\nu - E_g]^n \quad \text{---------} \quad (1)$$

where hν is the photon energy, h is Planck's constant, α is the absorption Coefficient, Eg is the optical energy gap, A is the constant, for direct transitions n=1/2. We plot a graph between $(\alpha h\nu)^2$ versus hν, the extrapolation of the straight line to $(\alpha h\nu)^2 = 0$ axis gives optical band gap. Figure 2 shows Tauc's plot for all the samples. Band gap for all the samples lie in the range of 1.86 ev to 2.21 ev and are mentioned in table 1.

Refractive index of material determines the speed of light in the material. It is an important constant for optoelectronic devises as it would responsible for the nature of interaction of the material with the opticalenergy incident on it. Refractive indexes of all the polymer samples were calculated according to the relation:

$$n = 3.3668\ E_g^{-0.32234} \quad \text{------ (2)}$$

The refractive indexes of all the samples have been listed in table 1. Absorption coefficients for all the polymer samples were calculated using the following relation:

$$\alpha = 2.303\ A/T \quad \text{-------- (3)}$$

Where T is thickness.

When optical energy interacts with matter, it scatters and loss occurs. These losses are described by extinction coefficient. The extinction coefficient denoted by K was calculated according to the equation:

$$K = \alpha\lambda/4\pi \quad \text{--------(4)}$$

Extinction coefficient as a function of wavelength is shown in figure 4.

The optical conductivity of all the samples were evaluated using the equation:

$$\sigma = \alpha nc/4 \quad \text{-------- (5)}$$

Optical conductivity as a function of energy is shown in figure 5.

Variation in optical constants with the amount of zinc doped in the material is shown in the figure 6.

IV. SEM Analysis

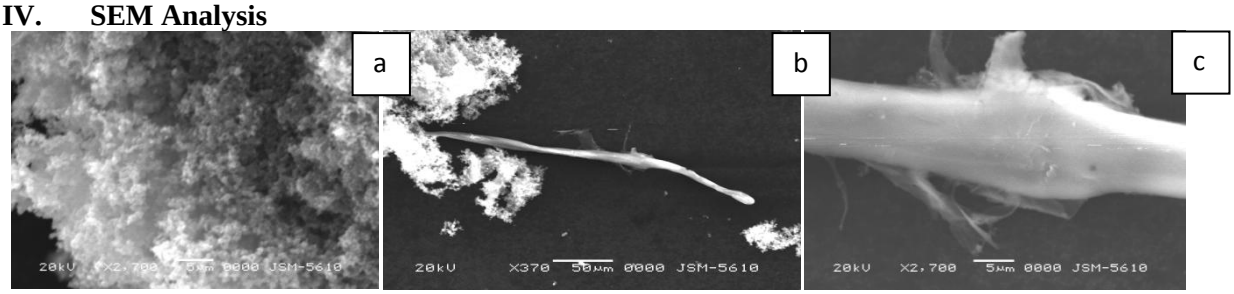

Figure 6: SEM micrographs of (a) 5% Zinc Doped polypyrrole (b),(c) 25% Zinc Doped polypyrrole.

Figure 6a shows the SEM micrographs of 5% zinc doped and figure 6b and 6c are SEM images of 25% zinc doped samples. It must be observed that at low doping level polymer shows spherical morphology but at higher doping levels formation of rods have been observed.

References

[1] H. Shirakawa, E. J. Louis, A. G. MacDiarmid, C. K. Chiang, A. J. Heeger. J. Chem. Soc., Chem. Commun. 578, 1977.

[2] T. A. Skotheim, R. L. Elsenbaumer, J. R. Reynolds (Ed.). Handbook of Conducting Polymers, 2nd ed., Marcel Dekker, New York 1998.

[3] P. Chandrasekhar. Conducting Polymers, Fundamentals and Applications: A Practical Approach, Kluwer Academic, Boston, 1999.

[4] H.S. Nalwa, Handbook of Organic Conductive Molecules and Polymers, Vols. 1–4, Wiley, New York, 1997.

[5] D. Fichou, Handbook of Oligo- and Polythiophenes, Wiley, New York, 1998.

[6] K. Muellen, G. Wegner, The Oligomer Approach, Wiley, New York, 1998.

[7] D.M. de Leeuw, P.A. Kraakman, P.F.G. Bongaerts, C.M.J. Mutsaers, D.B.M. Klaassen, Electroplating of conductive polymers for the metallization of insulators, Synth. Met. 66,263–273, 1994.