

## EVALUATION OF OPTICAL CONSTANTS OF WIDE BAND GAP CADMIUM DOPED POLYPYRROLE

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### 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. Cadmium was found to be an appropriate dopant. Cadmium belongs to group IIB with atomic number 48 having electronic configuration [Kr] 4d<sup>10</sup> 5s<sup>2</sup>. An expected substitution of Cd with Nitrogen of Pyrrole would leave a single electron with Cd after bond formation. Thus, creating a probability of polaron and bipolaron band formation. The expected results are reflected in the absorption spectra of the samples with clearly visible broad free carrier tails after 500 nm. Characteristic peak around 350 nm to 450nm is observed in all the samples confirming the formation of polypyrrole. Band gap of samples are found in the range of 2.80 eV to 4.07 eV. Apart from this some of the important optical constant 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. SEM analysis reveals formation of highly spherical polypyrrole with high amount of porosity.

**KEYWORDS:** Absorption Coefficient, Extinction Coefficient, Refractive Index, Optical Conductivity, Dielectric Constant

### INTRODUCTION

Polymers shape our lives because polymers can be shaped. Until about 30 years ago all carbon based polymers were rigidly regarded as insulators. The idea that plastics could be made to conduct electricity would have been considered to be absurd. Indeed, plastics have been extensively used by the electronics industry because of this very property. They were utilized as inactive packaging and insulating material. This very narrow perspective is rapidly changing as a new class of polymer known as intrinsically conductive polymer or electro active polymers are being discovered. Each polymer type has already found widespread use in many, mainly optical and electronic applications such as batteries, displays, plastic wires, optical signal processing, information storage, solar energy conversion, etc. In recent years, intrinsic conducting polymers with conjugated double bonds have attracted much attention as advanced materials.

Among those conducting polymers, polypyrrole (PPy) is especially promising for commercial applications because of its good environmental stability, facile synthesis and higher conductivity than many other conducting polymers. PPy can often be used as biosensors [1, 2], gas sensors [3, 4], anti electrostatic coatings, solid electrolytic capacitor. Polypyrrole can be prepared by chemical or electrochemical oxidation of Pyrrole in various organic solvent and in aqueous media [5, 7]. Although electrochemical polymerization leads to formation of a conductive PPy thin film on the working electrode, it is not appropriate for the mass production.

In contrast, chemical oxidative polymerization is simple, fast, cheap, and easily scaled up. In a typical chemical oxidative polymerization of PPy, many oxidants, such as ferric perchlorate, ferric chloride and ammonium peroxydisulfate have been used [8].

The properties of fabricated conducting polymers are strongly dependent on the preparation conditions and various additives introduced into reaction mixture [9, 10]. The basic purpose of this work was to study the optical properties of polypyrrole for its use in optoelectronic devices. Various optical constants that would determine the interaction of optical energy with polymer such as absorption coefficient, extinction coefficient, refractive index and optical conductivity are evaluated.

## EXPERIMENTAL

Pyrrole monomer was purchased from sigma Aldrich and was used as received. Analytical grade Ferric chloride and cadmium nitrate were purchased from qyalings and were used as received. 1.42 grams of  $\text{FeCl}_3$  was dissolved in 50ml 1M HCl at 5 °C 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 cadmium, cadmium nitrate in different molar ratios was added to Pyrrole monomer and ultrasonicated for 15 mins. Cadmium was doped in molar ratios of 5%, 10%, 15%, 20% and 25%.

## RESULTS AND DISCUSSIONS

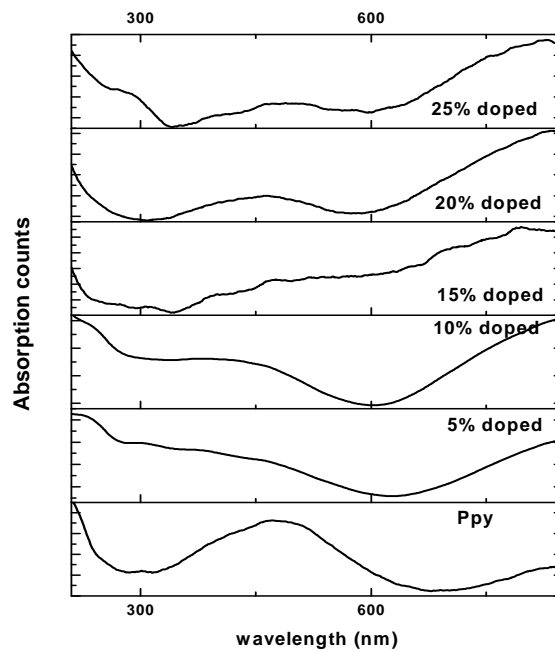
### UV-Vis Spectroscopy

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 shows these absorption spectra. A major peak at 472 nm (2.62eV) was observed for undoped polypyrrole which is attributed to  $\pi$ - $\pi^*$  inter band transitions and is a characteristic peak of conducting polypyrrole. Shoulder at 223 nm (5.55 eV) is also observed.

This tiny shoulder is shifted to 235 nm (5.27 eV) when the material is doped with 10% Cd. Although this peak vanishes when polymer is doped with 20% Cadmium. A small hump at 851 nm (1.45 eV) indicating polaron bipolaron transitions for polypyrrole faces a shift to 882 nm (1.40 eV) for 10% doped sample and 860 nm (1.44 eV) for 20% doped sample. The characteristic peaks for these samples are observed at around 382 nm (3.24 eV) and 462 nm (2.68 eV) for 10% and 20% doped samples respectively.

Thus a considerable shift in wavelength is observed after doping. These observed shifts are due to dopant-polymer interaction. Polypyrrole doped with 5%, 15% and 25% cadmium no peaks were observed. Instead the spectra show continuous absorption with intense shoulders indicating formation of polaron bipolaron bands.

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  $\pi$ - $\pi^*$  electronic transition [11]. Thereafter up till 496 nm the absorption peaks indicate the polaron transitions. The peak around 750 nm in polypyrrole spectrum has been assigned to  $-\text{NH}-$  species, which are generated during doping [11]. For the samples with 5%, 15% and 25% doped samples, humps observed after 500 nm up till 900nm can be called the broad free carrier band.

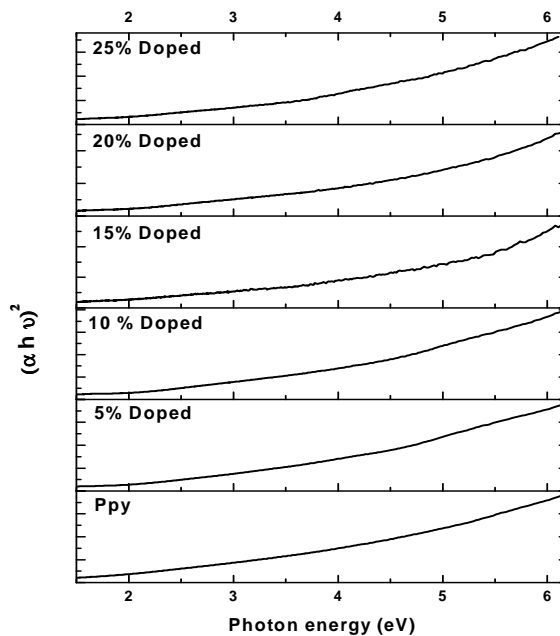


**Figure 1: Absorption Spectra of the Samples**

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 [12].

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

where  $h\nu$  is the photon energy,  $h$  is Planck's constant,  $\alpha$  is the absorption Coefficient,  $E_g$  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  $h\nu$ , 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.



**Figure 2: Tauc's Plot for Determination of Band Gap**

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

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

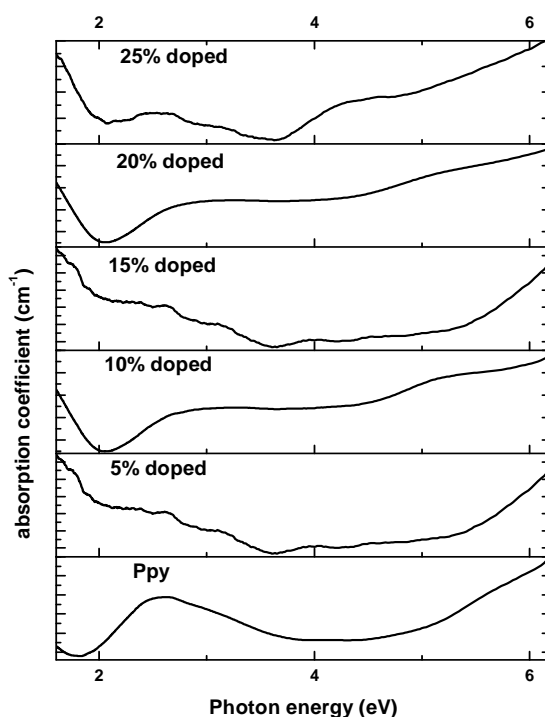
The refractive indexes of all the samples have been listed in table 1. The absorption coefficient,  $\alpha$ , is a property of a material which defines the amount of light absorbed by it. The inverse of the absorption coefficient is the average distance traveled by a photon before it gets absorbed. We classify materials as opaque, translucent and transparent according to the absorption strength of these materials. Thus absorption coefficient is an important factor for optoelectronic devices. Absorption coefficients for all the polymer samples were calculated using the following relation:

$$\alpha = 2.303 A/T \quad (3)$$

Where T is thickness

**Table 1: Evaluated Optical Constants**

Amount of Cd	Refractive Index	Absorption Coefficient	Extinction Coefficient ( $\times 10^{-5}$ )	Optical Conductivity ( $\times 10^{10}$ )	Optical Band Gap (eV)
0%	2.75	4.94	2.62	3.24	2.83
5%	2.72	4.28	2.19	2.78	2.75
10%	2.69	1.95	0.96	1.25	2.80
15%	2.75	0.61	0.32	0.40	4.07
20%	2.74	1.23	0.64	0.80	3.38
25%	2.60	1.45	0.64	0.90	3.21



**Figure 3: Absorption Coefficient as a Function of Energy**

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:

$$K = \alpha \lambda / 4 \pi \quad (4)$$

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

Optical conductivity is one of the powerful tools for studying the electronic states in materials. If a system is subjected to an external electric field then, in general, a redistribution of charges occurs and currents are induced. The optical conductivity of all the samples were evaluated using the equation:

$$\sigma = \alpha n c / 4 \pi \quad (5)$$

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

For high speed data transmission, effective dielectric constant plays an important role. Theoretical models have been developed to study dielectric constants for the applications of material in optoelectronic devises.

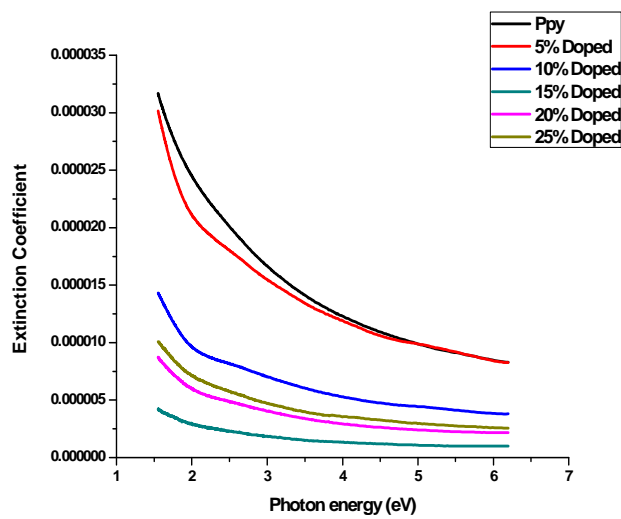


Figure 4: Extinction Coefficient as a Function of Energy

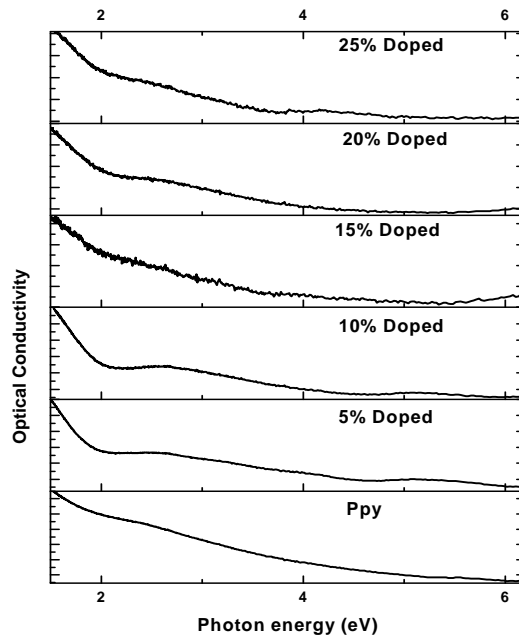


Figure 5: Optical Conductivity as a Function of Energy

In the present work the dielectric properties of the materials were investigated. Figure 6 shows the variation in the Imaginary of dielectric constant as a function of energy. The dielectric constants were evaluated as using the equation:

$$\text{Imaginary part: } \epsilon_i = 2nK \quad (6)$$

$$\text{Real part: } \epsilon_r = n^2 - K^2 \quad (7)$$

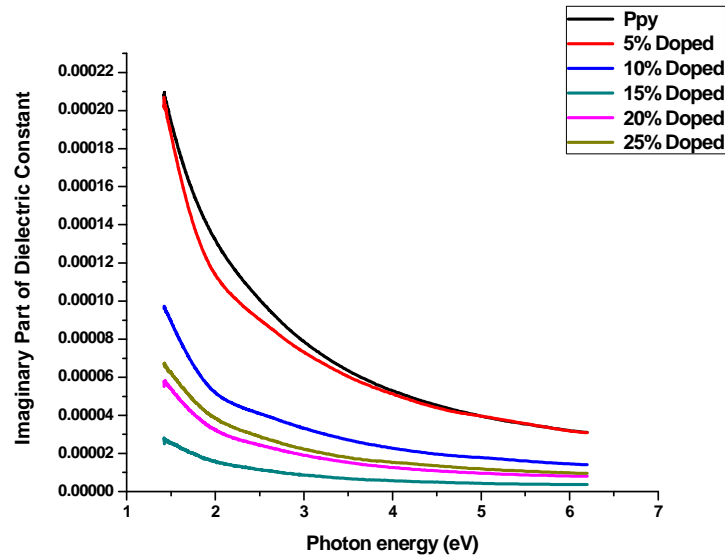


Figure 6: Imaginary Part of Dielectric Constant as a Function of Energy

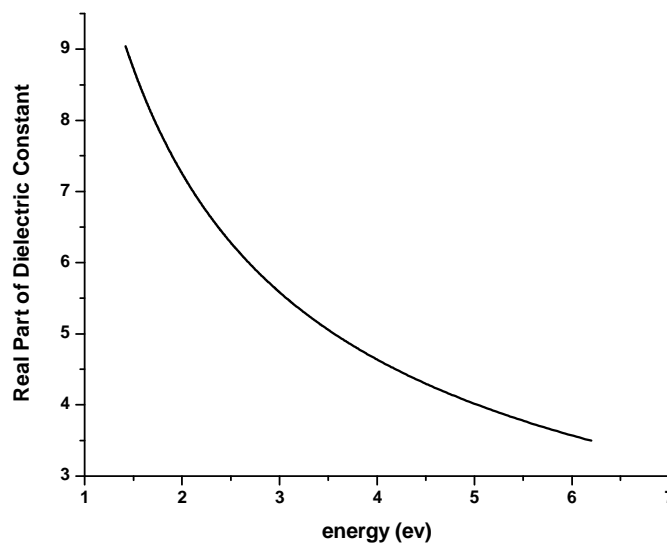
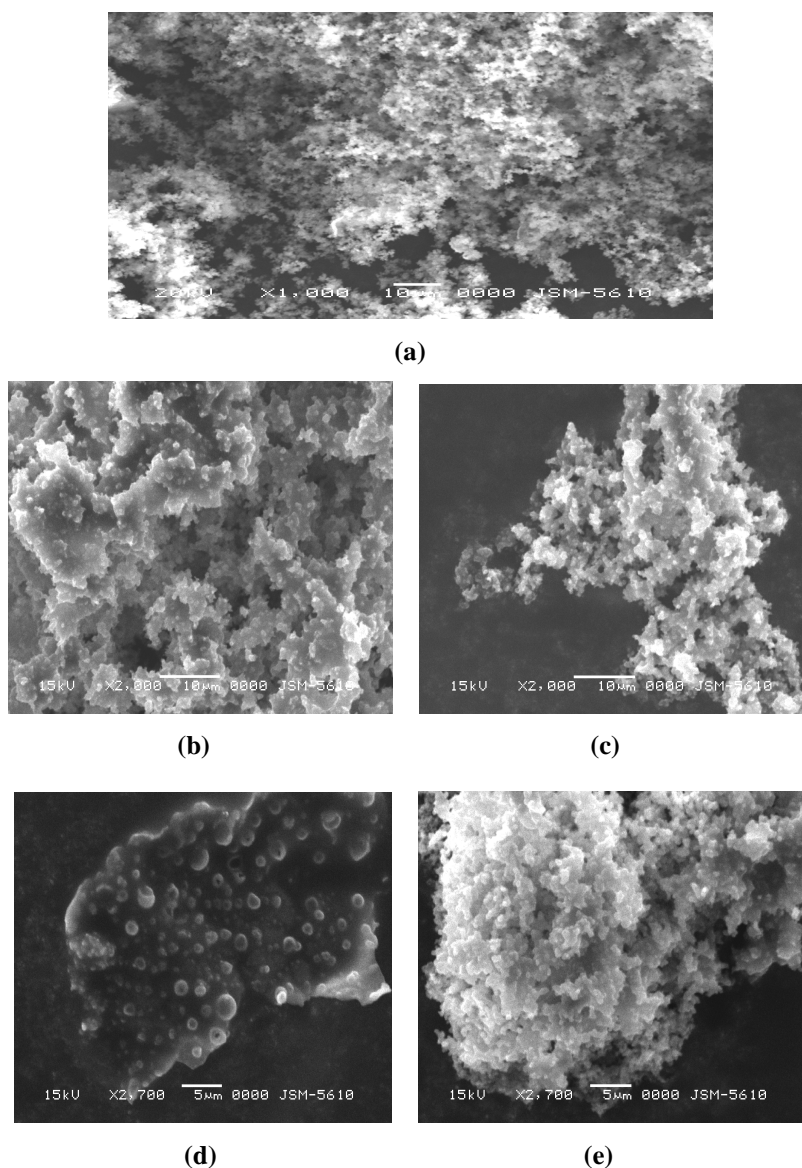


Figure 7: Real Part of Dielectric Constant as a Function of Energy

The value of the Extinction Coefficient lies in the order of  $10^{-6}$  where as the refractive index has a comparative very low value. Hence no major change would be observed in the values of the real part of the dielectric constant for any of the samples and so all the samples would exhibit a similar variation in real part with respect to energy. This variation is shown in figure 7.

## SEM Analysis



**Figure 8: SEM Images of (a) Polypyrrole, (b) (c) 15% Doped Polypyrrole, (d) 20% Doped Polypyrrole, (e) 25% Doped Polypyrrole**

## CONCLUSIONS

The optical properties of Cadmium doped polypyrrole have been investigated and the optical constants have been evaluated. It can be observed that the band gap of all the samples lie in the range of wide band gap semiconductors. The values of the band gap are found to be higher than the reported values. This rise in band gap is attributed to formation of polaron-bipolaron bands in the intermediate space between valance and conduction band. The refractive index of all the samples lie in the range of 2.6 to 2.7 and the variation with doping of cadmium is shown in figure 8. The optical conductivity of the sample decreases with increase in the amount of dopant but, a similar variation in the extinction coefficient indicates that with rise in the amount of the Cd the scattering losses would also decrease. It must also be noted that samples are found to absorb light in the three major portions of the electromagnetic spectrum i.e. ultra violet, visible and near IR regions. Thus material can efficiently be used as a coating material on photoelectric material.

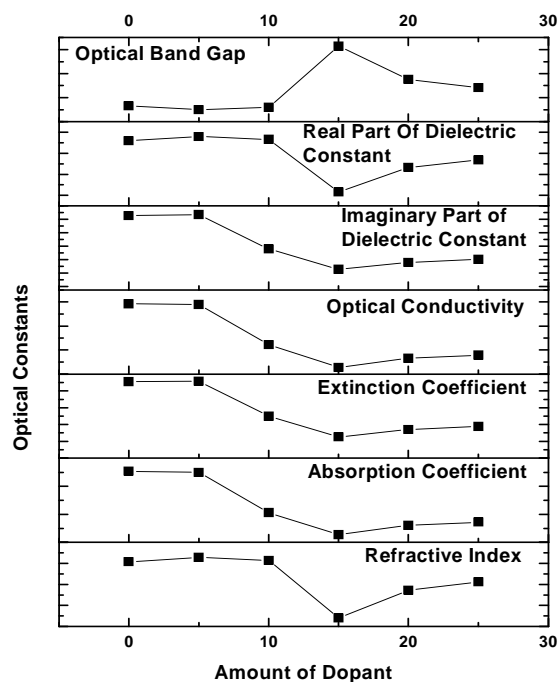


Figure 9: Variation in the Optical Constants with Amount of Dopant

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