Interaction of Titanium salt and Polyaniline (PANI): Study of Band Gap

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ABSTRACT

The present work envisages the synthesis of polyaniline and its doping with salt of a transition metal (Titanium) and effect of dopant on its optical properties to study changes in band gap. Polyaniline was synthesized by process of chemical oxidative polymerization. Chemical Doping of the dopant has been carried out in synthesized polyaniline by making different concentration of dopant in neutral medium and using THF as solvent. An effort has been done to see the effect of dopant in polyaniline by its properties characterized by UV-Visible spectroscopy and then determining band gap with the help of UV spectra.. A significant change has been observed after doping. UV-Visible study shows that optical parameters change after doping. The study reveals that strong dopant interaction takes place with polyaniline network which is responsible for observed changes.

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Introduction

Much of the interest in conducting polymers arises from their potential applications in many areas especially in electronic devices fabrication viz., rechargeable battery, sensors, (LEDs) etc. [1, 2]. Due to diversified utilization of conducting polymers [3], researchers are now focusing the much attention to develop lightweight materials and in small size as nano for advance technology. Due to a unique combination of properties, now a days, the most extensively studied conducting polymer systems are based on polythiophene and its derivatives [4, 5, and 6], polypyrrole, and polyaniline, which make them attractive alternatives for certain materials currently used in microelectronics. From the fundamental point of view, dielectric properties are of great importance for heterogeneous nature of conducting polymers [7, 8] in designing electronic devices. One of the important conducting polymers, polyaniline (PANI) has shown good thermal stability and high environmental stability. It is also able to gain certain amount of water to attain the maximum conductivity in both undoped and doped states. These polymers are made conductive by reacting conjugated semiconducting polymers with an oxidizing agent, a reducing agent or a protonic acid resulting in highly delocalized polycations or polyanions. The further evidence and possibility of structural formation of PANI – with some salts as earlier oxidation / protonation states of polyaniline has been supported [9], π-conjugation backbone of organic polymers, which favor the chemical doping mechanism. Conjugated polymers have relatively large band gap, the concentration of free carriers is very low at normal temperature. Doping approach generates higher carrier's concentration in conjugated polymers; polyaniline is a known polymer to exhibit interesting electrical conductivity. In this work, chemical doping of synthesized polyaniline has been done with different concentration of Titanium nitride (dopant) in aqueous tetrahydrofuran (THF) solution. Although, vast researches work, reported on polyaniline, But still there is a draw back with this π- conjugated polyaniline (PANI) due to

its poor mechanical strength, less solubility in solvents, which lead the problem of proper product processing for application purpose. Recently, we have studied on chemical doping of metal salts in polyaniline and the measurements of electrical and dielectric properties [10-11], which have shown the effective efficiency of chemical doping and stability of metal salt dopant. In the present investigation, we have studied optical properties of TiN doped polyaniline. We have also observed the influence of dopant in terms of band gap in doped polyaniline.

Experimental

Chemicals

Aniline (Qualigens Fine Chemical Ltd. Bombay L.R. Grade), ammonium per sulfate (S.D Fine Chemicals Ltd. Bombay L. R. Grade), hydrochloric acid (Qualigens Fine Chemicals Ltd. Bombay L. R. Grade), ammonia solution in water 28% (S.D. Fine Chemicals Ltd. Bombay L.R. Grade),tetrahydrofuran (THF) (Merck India Ltd. Bombay. L.R. Grade), TiN (LR grade, 99.5% purity, HiMedia Laboratories Pvt. Ltd. Mumbai.

Synthesis and Doping of Polyaniline

The polyaniline (PANI) has synthesized by the method suggested by A G Mac Diarmid et al. [12]. Doping agent TiN has been used with different concentration such as 10.0, 15.0 and 20.0 % (w/w) in the solvent tetrahydrofuran (THF) for doping of synthesized polyaniline. After 12 h. the polyaniline-dopant mixture was filtered to achieve doped polyaniline and was made moisture free in oven at 80^0C for 24 h. Then all the samples were well ground to make fine powder and UV-Vis spectra was analysed.

Results and discussion

Optical Characterization

Pure PANI was doped with TiN and then UV spectra of doped samples was noticed. There was decrease in intensity of absorption after doping which shows interaction of dopant with the polymers. The spectra are shown in Fig. 1
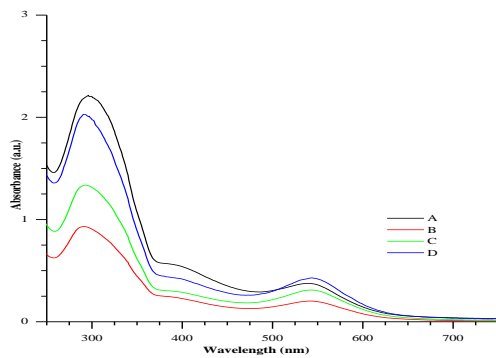

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Fig 1. UV-Vis spectra of Pure PANI (A), and 10 %(B), 15% (C) & 20 % (D) TiN doped PANI.

In a semiconductor bulk solid, the transitions occur between the valence band and the conduction band. The valence band and conduction band are the solid-state analogue of the highest occupied molecular orbitals, HOMO and the lowest unoccupied molecular orbitals, LUMO of molecules. E_g is the band gap or energy difference between the valence and conduction band. In many organic materials, it is usual to analyze the optical absorption at the fundamental edge in terms of band-to-band transitions theory [13].

Optical parameters such as absorption coefficient (α), extinction coefficient (k) and energy band gap (E_g) have been determined for undoped and doped PANI samples at 298K through absorption spectra. The optical absorption coefficient (α) has been determined from the absorption spectra using Eq. (1). After correction for reflection, the absorption coefficient (α) has been calculated from the absorbance (A), using the relation:

$$I = I_0 \exp(-\alpha x) \qquad (1)$$

The Eq. (1) may be written as:

$$\alpha = 2.303/x \log(I/I_0) = [2.303/x] A \qquad (2)$$

where x is the thickness of the sample.

$$\alpha = 2.303 (A/d) \qquad (3)$$

where A is the absorbance and d is the thickness of the quartz cuvette used for the UV–Vis experiments. The relationship between the optical band gap (E_g), absorption coefficient (α) and the incident photon energy (hν) is given by Eq. (4) [14-17].

$$\alpha h\nu \propto (h\nu - E_g)^n \qquad (4)$$

In case of TiN doped PANI, Values of direct band gaps are 3.42 eV, 3.05 eV and 3.25 eV for undoped, 10% and 15 % doped PANI and no slope is observed for 20% doped PANI. Interestingly, value of direct band gap is less for 10% doped but more for 15% doped PANI, which may be due to more interaction of metal ions with the polymer at low concentration.
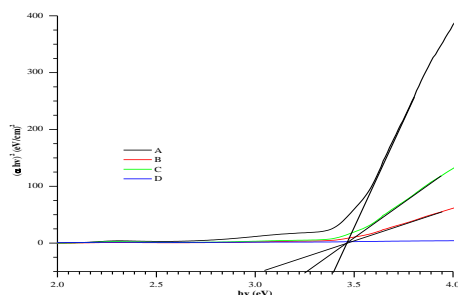

Fig 2. Optical band gap (Direct) of PANI (A) and PANI doped with 10 %(B), 15% (C) and 20 %(D) concentration of TiN.
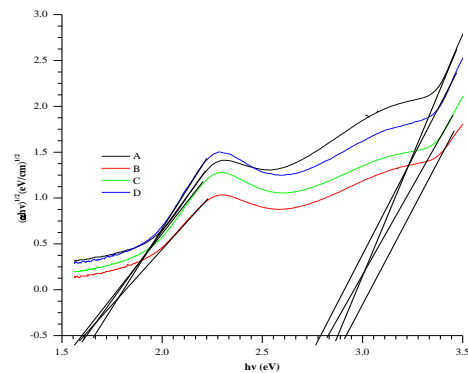

Fig 3. Optical band gap (Indirect) of PANI(A) and PANI doped with 10 %(B), % (C) and 20 % (D) concentration of TiN.

Table 1. Values of Band Gaps, Absorption coeff. and Extinction coeff. for PANI doped with TiN.

Dopant conc. in (w/w)	Direct band gap E_g (eV)	Indirect band gap E_g (eV)	Absorption coeff. α at λ=280 nm	Extinction Coeff. k at λ=280 nm
Undoped	3.42	2.86, 1.62	4.56	101.55
10% doped	3.05	2.81, 1.53	1.98	44.1
15% doped	3.25	2.86, 1.56	2.8	62.35
20% doped	No slope	2.74, 1.64	4.22	93.97

Values of Direct and Indirect band gaps are shown in Fig. 2 & Fig.3 and Table 1 shows values of absorption and extinction coefficient.

Conclusion

Optical band gap in PANI decreases with increasing content of the metal salts and hence optical conductivity increases.

Experimental results of optical absorption fit well by the Maxwell-Garnet model. Electrical conductivity of the conducting polymers can be increased by doping of suitable metal salts. So, this is a simple way by which optical and electrical properties of other conducting polymers may be enhanced by using different concentrations of dopant.

From the structural study it is found that PANI is highly cross linked in all the pure and doped states. The UV-Vis absorption peak at 375 nm reveals the formation of polaronic structure due to doping of metal salts. The optical band gap of the pure PANI is found to decrease in the doped PANI due to the formation of polaronic structure. The optical band gap of the PANI depends on the extended conjugation, oxidation level and doping.

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