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Influence of Dopant on Optical Properties of Conducting Polymers

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Abstract- Polyaniline (PANI) was prepared and then doped with magnesium perchlorate in different concentration. Optical, sptructural and spectroscopic studies of magnesium perchlorate [Mg $(ClO_4)_2$] doped PANI have been studied at different concentration of dopant. UV-vis, Photoluminescence, FTIR, DC conductivity and SEM techniques were used for optical, structural, electrical and morphological characterization of the prepared conducting doped polymer PANI. The UV-vis spectra shows appreciable decrease in band gap after doping which is also confirmed by increase in DC conductivity with increase in concentration of dopant.

Keywords: Doping, Conducting polymers, Photoluminescence, Band-gap.

1. INTRODUCTION

Polymers were basically thought to be insulators till two and a half decades ago and then a new class of polymers was synthesized known as conducting polymers. Much of the interest in conducting polymers arises from their potential applications in many areas especially fabrication of electronic devices like rechargeable battery, sensors, LEDs etc. [Frolov (1998), Polson (2004)]. Now days, the most extensively studied conducting polymer systems are polythiophene [Iraqi (1998), Ng (1999), Zhai (2003)] polypyrrole, and Polyaniline (PANI), due to their unique properties. One of these conducting polymers, PANI has shown good thermal 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. Conjugated semiconducting polymers are made conductive by reacting them with an oxidizing agent, a reducing agent or a protonic acid resulting in highly delocalized polycations or polyanions. The evidence and possibility of structural formation of hybrid materials of PANI with some metal salts has been illustrated [Samui (2003)]. PANI is a well known conducting polymer which shows interesting electrical conductivity. In the present work, chemical doping of synthesized PANI has been done with different concentration of magnesium perchlorate i.e. [Mg $(ClO_4)_2$] (dopant) in aqueous tetrahydrofuran (THF) solution. Researchers have reported work on chemical doping of metal salts in PANI and the measurements of optical and spectroscopic properties [Ali (2006), Kasim (2006)], which shows the effective efficiency of chemical doping and stability of metal salt dopant. In the present investigation, we have studied the [Mg $(ClO_4)_2$] doped PANI and also observed the influence of different concentration of dopant in terms of optical properties in doped PANI.

2. EXPERIMENTAL DETAILS

2.1. Chemicals Used

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 28.0% (S.D. Fine Chemicals Ltd. Bombay L.R. Grade),THF (Merck India Ltd. Bombay. L.R. Grade), magnesium perchlorate (L.R. grade, G. Frederick Smith Chemicals Columbus, Ohio, USA), polyvinyl chloride (PVC) L.R. grade (Danpha Chemicals Bombay, India, and dioctylphthalate (L.R. grade, Loba Chemicalas Bombay, India).

2.2. Synthesis and Doping of PANI

The PANI was synthesized by the method suggested by Mac Diarmid et al. [1986]. Doping agent [Mg $(ClO_4)_2$] has been used with different concentrations such as 5.0, 10.0, 15.0 and 20.0 % (w/w) in the solvent mixture of water and THF solution (4: 6 v/v), for doping of synthesized PANI. After 12 h of equilibration the PANI- dopant mixture was filtered to achieve doped PANI and kept in an oven maintained at a constant temperature of 80^0C for 24 h for complete drying.

3. RESULTS AND DISCUSSION

Fig.1 shows the UV spectra of PANI with different concentration of [Mg $(ClO_4)_2$] as dopant. From Fig. 1

it is clearly seen that with lower concentration of dopant [Mg $(ClO_4)_2$], there is decrease in intensity of absorption (hypochromic shift) but as soon as the concentration of dopant is increased, there is increase in intensity again, although it is never more than that of pure polymer.

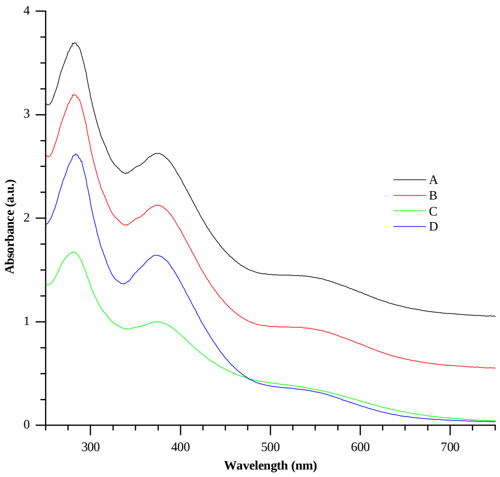

Fig. 1. UV-Vis spectra of Pure PANI (A), 5%(B),10%(C) and 15% (D) [Mg $(ClO_4)_2$] doped PANI.

It has been observed that in case of doping with [Mg $(ClO_4)_2$], values of direct and indirect band gaps are less for doped PANI than that of undoped PANI (Direct band gap 3.56 eV for undoped, 3.48 eV for 5 and 10 % doped, and 3.27 eV for 15 % doped) second set of band gap 2.71 eV for undoped, 5 % and 10 % doped, 2.44 eV for 15 % doped).

Indiect band gap is 2.02 eV for undoped, 5 % and 10 % doped PANI and 1.56 eV for 15 % doped PANI.

Hence, it is clearly indicated that indirect band gap is always less than direct band gap.

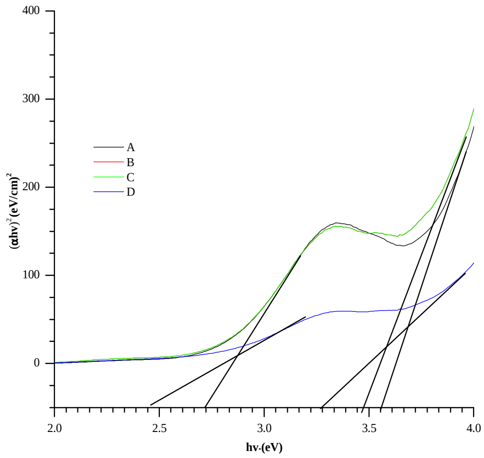

Fig. 2. Optical band gap (Direct) of PANI (A) and PANI doped with 5 %(B), 10% (C) and 15 %(D) concentration of [Mg $(ClO_4)_2$].

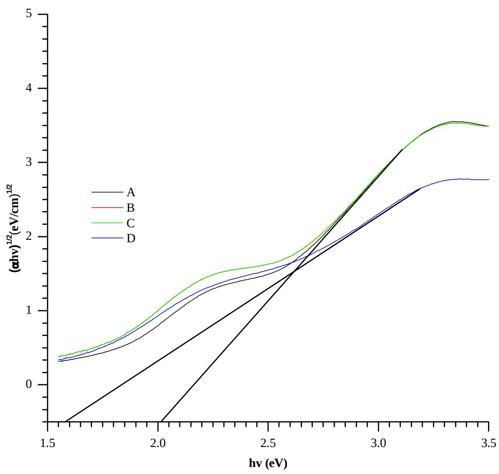

Fig. 3. Optical band gap (Indirect) of PANI (A) and PANI doped with 5 %(B), 10% (C) and 15 %(D) concentration of [Mg $(ClO_4)_2$].

Table 1. Values of Band Gaps, Absorption coeff. and Extinction coeff. for PANI doped with $[Mg(ClO_4)_2]$.

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	3.56, 2.71	2.02	8.49	189.07
5% doped	3.48, 2.71	2.02	7.34	163.46
10% doped	3.48, 2.71	2.02	3.85	85.73
15% doped	3.27, 2.44	1.56	5.97	132.95

4. CONCLUSION

Optical band gap 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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