Bio - Sensing Property of Poly-Aniline Thin Films Doped with HCL for Ammonia Detection at Room Temperature.

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In the present paper the conducting polymer polyaniline were in-situ synthesized by chemical polymerization. The polyaniline thin films are formed with the help of chemical bath deposition technique. The physico-chemical characterization of prepared conducting polymer is done with UV-Visible and FTIR spectroscopy. FTIR spectroscopy revealed formation of Polyaniline. The electrical characterization gives the conductivity of the thin films; conductivity of polyaniline film is in very good agreement with the available reported data base. The prepared polyaniline thin film is used as an active layer in bio-sensors to sense the ammonia. The electrical conductivity of polyaniline show significant change when it irradiate with ammonia vapours. As the concentration of ammonia vapour increases the resistance is found to be increase. Several orders of magnitude of change in resistance are observed upon chemical doping and dedoping of the polyaniline, when expose to the ammonia. This large conductivity range can be utilized to make sensitive chemical sensors. It has been observed that these films are selective for ammonia gas. Hence polyaniline films can be used as ammonia sensors at room temperature. Further the response of sensitivity can be studied. This study may reveals that the thin films of Polyaniline possess response time to Ammonia significant.

Key word: Polyaniline, CBD, Ammonia

Introduction

Interest in the development of Polyaniline, Polypyrrole, Polythiophene, Polyphenylene and other conducting polymers has increased tremendously in recent years. Electrically conducting polymers described as a new class of '*synthetic metals*' reached a high interest in the past few years, confirmed by the **2000 Nobel Prize in chemistry** for the discovery and development of conductive polymers (Alan J. Heeger, Alan G. MacDiarmid and Hideki Shirakawa) [1].

A key property of a conductive polymer is the presence of conjugated double bonds along the backbone of the polymer. In conjugation, the bonds between the carbon atoms are alternately single and double. Every bond contains a localized "sigma" (σ) bond which forms a strong chemical bond. In addition, every double bond also contains a less strongly localized "Pi" (π) bond which is weaker. However, conjugation is not enough to make the polymer material conductive. Further to overcome the limitations there is need of doping of protonic acid which makes them more conductive.

The most commonly studied classes of conducting polymer were Polyacetylene, Polythiophene, Polypyrrole, Polyaniline and their derivatives, being investigated as conducting matrices for electronics applications such as Functional electrodes, Electrochromic devices, Optical switching devices, Batteries, TFTS, OLED, Sensors and so on [2]. Among all theses conducting polymer, Polyaniline (PANI) is one of the most significant material because of its high conductivity upon doping with acids, well behaved electrochemistry, and easy preparation under reproducible conditions by electro chemical polymerization and chemically oxidation of aniline, chemical and electrical stability and good environmental stability [2, 3].

If we look for the other members of this class (e.g. Polythiophene, Polypyrrole, and Polyacetylene) the conducting mechanisms are well understood by considering their conjugated carbon backbones, the conducting mechanism in the polyaniline forms is more complex. Polyaniline acts as an electrically conductive material only in the protonation form of emeraldine salt. It can changes the electronic conductivity about 10's orders of magnitude, passing from insulating state (e.g. emeraldine base with $\sigma<10^{-10}$ S/cm^{-1}) to metallic conduction (e.g. emeraldine salt with $\sigma\sim10^{-1}$-$10^{-2}S/cm^{-1}$), depending upon the degree of doping/protonation [4-6].

The efficient polymerization of aniline is achieved only in an acidic medium, where aniline exists as an anilinium cation. A variety of inorganic and organic acids of different concentration have been used in the syntheses of PANI; the resulting PANI, protonated with various acids, differs in solubility, conductivity, and stability [7-9]. For the present paper, we have selected hydrochloric acid in equimolar proportion to aniline, i.e., aniline hydrochloride was used as a monomer. The handling of solid aniline salt is preferred to liquid aniline from the point of view of toxic hazards. Peroxydisulfate is the most commonly used oxidant, and its ammonium salt was preferred to the potassium counterpart because of its better solubility in water. [10-13].

In the thin film of Polyaniline, the properties of film depends on a number of important parameters, such as the type of solvent and their molar concentrations, temperature and on other synthesis conditions, research is still continuing on the preparation and characterization of conducting polymers. Hence, in the present paper effort has been made to investigate the electrical, optical and structural properties of conducting polymer Polyaniline on a particular 5^0C temperature, by chemical polymerization process [14–16]. In the following sections, the second section of this paper deals with the experimental section in which the first part illustrates the detail of chemicals and instruments used for the formation and characterization of the conducting polymer film, the second gives the steps involving in the synthesis of PANI and the later part gives the preparation of PANI film with the help of spin coater. The Result are Discussed in the third section and fourth section conclude this paper.

2. EXPERIMENTAL.

2.1 Materials and Equipment:

All the chemicals and solvents used were dried and purified by standard methods. Analytical grade Aniline Hydrochloride (Ranbaxy New Delhi), Ammonium peroxidisulphate (APS) and Hydrochloric acid (HCL) (SD - fine chem.), Acetone and DMF are (Loba chemicals) and for filtration of precipitate what man's filter paper No.60 are used.

The Polyaniline films produced were characterized by FTIR spectroscopy (Nicolet-380), UV-spectrophotometer (SHIMADZU-1601), X-ray diffractometer (XRD) Raigaku, Japan And Conductivity measurement is done by the two-probe technique.

2.2 Synthesis of conducting polymer;

In present paper the conducting polymer is synthesized by chemical method by oxidizing the corresponding monomer. The thin film of polyaniline has been prepared successfully by chemical oxidatiative polymerization and Sol-Gel technique. The physical properties of the film are characterized by the FTIR spectroscopy; the FTIR spectroscopy gives details of stretching bond in the prepared polymer film. The UV-vis spectrum is useful for gauging the extent of conjugation - highly conjugated, providing information about the extent of conjugation, the electronic spectrum is indicative of polymer morphology, the presence of a free carrier tail. The XRD technique is useful for structural investigation. The change in conductivity due to temperature variations were observed with two probe method at room temperature.

To oxidized 0.2M Aniline hydrochloride with 0.25M Ammonium peroxidisulphate aqueous medium Aniline Hydrochloride (purum: 2.5 gram, 20 mmole) was dissolved in deionized water in volumetric flask to 50 ml. of solution. Ammonium peroxidisulphate (purum: 5.79gram, 2.5 mmole) was dissolved in deionized water in volumetric flask to 50 ml. of solution. Both solutions are kept below room temperature for 1 hour, then mixed in beaker, electromagnetic stirrer for 3.5 hour and left to polymerize. The polymerization was carried out in a temperature controlled water bath for 24hour at 5^0C. Next day Polyaniline precipitate was formed and collected on Whatman's filter paper, washed with three 100 ml portion of 0.2M HCL and thereafter with Acetone. Polyaniline (emerdine) powder was formed. This powder was immersed in 0.1 M NH_4OH and washed and dried in air and vaco at 60^0 C. [17]. Oxidation of aniline hydrochloride with ammonium Peroxidisulphate yields Polyaniline [18, 19] as shown in Figure.1

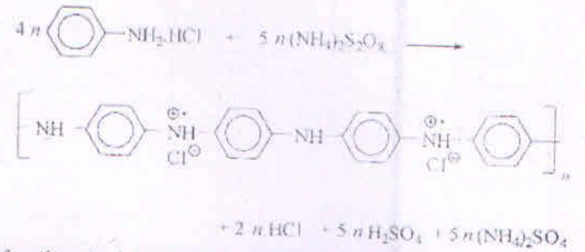

Fig.1 Oxidation of aniline hydrochloride with ammonium peroxydisulfate yields Polyaniline (emeraldine) hydrochloride.

2.3 Formation of the polymer thin film:

For the measurement of conductivity, the film of Polyaniline is deposited by spin coating technique. In this process, the purified polymer was dissolved in DMF to form the Gel. The Polyaniline emerdine salt will dissolve in DMF with 0.5g: 10 ml with 3 hrs stirring. The solution of Polyaniline is spread on rotating substrate, repeating this process for two / three times the uniform film will be obtained. After evaporation of solvent a thin film is formed. During the deposition of the film the temperature of the spinning machine assembly and surrounding is maintained below the room temperature throught the deposition process. Initially the speed of machine is at the 500 rpm for 20 seconds and 1200 rpm for 50 seconds [10].

3. RESULT AND DISCUSSION.

The synthesized PANI films with optimized concentration of monomer, dopant, and oxidant prepared at a specific temperature 5^0C are subjected to study the electrical, optical and structural properties of (PANI). The conductivity of resulting film is studied by the two probe method. The optical property of PANI films were characterized by analyzing UV-Visible spectroscopy. The physical and structural properties of synthesized film are studied by FTIR spectroscopy and X-Ray Diffraction technique.

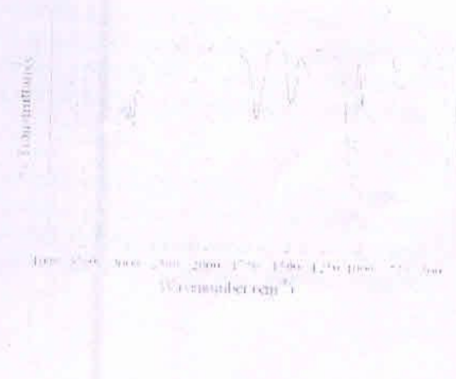

Figure-2
I-V Characteristics of PANI film.

Figure-3
FTIR spectra of PANI film.

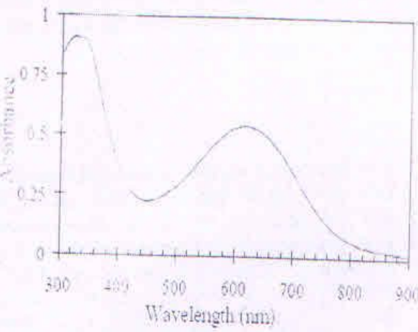

Figure-4
UV –Visible absorption spectra of PANI film

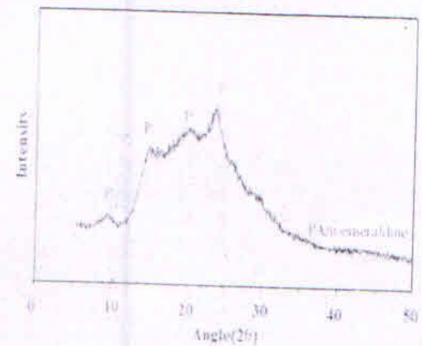

Figure-5
XRD patterns of PANI film.

3.1 Electrical characterization

The Fig-2 shows the I-V Characteristics of the synthesized PANI film. The electrical characterization of film is done by the two-probe method at room temperature. The current-voltage (I–V) characteristics of the synthesized PANI film are studied to ensure the ohmic behavior of the film. The I-V characteristic shows a linear relationship of PANI film .As we increase the applied voltage the current is increases in proportion with voltage, which reveals that the thin film of polyaniline has an ohmic behavior. This characteristic gives the thin film has conductivity in millamperes.

3.2 FTIR Analysis of synthesized PANI films:

The Figure-3 shows the FTIR spectroscopy of the synthesized PANI film. The molecular structure of the synthesized PANI film was studied using the FTIR spectroscopy. Formation of the polymers, presence of a functional group on the polymer backbone or change in the protonation -deprotonation equilibrium of emeraldine can be deduced from the presence of corresponding bands in the FTIR spectrum.It is seen that Quinoid and Benzenoid ring stretching bands are present at 1653 cm^{-1} and 1423 cm^{-1}. The C-H in plane and C-H out of plane bending vibrations appears at 1024 cm^{-1} and 952 cm^{-1}. The peak at 1315 cm^{-1} is assigned to C–N stretching of secondary aromatic amine. In addition, a relative weak peak at 1700 cm^{-1} appears in the spectrum is due to the stretching vibration of carbonyl group and it shows presence of AA in the film. Band at 3440 cm^{-1} is assigned to the N-H stretching band. All these characteristic bands confirm the presence of conducting ES phase of the polymer. This shows very good agreement with earlier reported work [20-22].

3.3 UV-Visible analysis of synthesized PANI films:

The Figure -3 shows the UV –Visible absorption spectrum of the synthesized PANI film. The peak at 320nm corresponds to the π-π^* transition of the Benzenoid ring, while the sharp trough at 440nm can be assigned to the localized polaron which are characteristics of the protonated Polyaniline, together with extended tail at 800nm representing the conducting ES state of Polyaniline.[23]

3.4 XRD Analysis of synthesized PANI films:

The figure-5 shows the XRD patterns of the synthesized PANI film. The main peaks in the XRD patterns of the Pani which is characteristics of the orthorhombic crystalline structure of the ES of Pani appeared in the position (2θ) of approximately 9.4, 15.1, 20.4 and 24.6which is good agreement with the reported **Haibing Xia et al**. The XRD patterns suggest linearization of the Pani Chain [24].