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Polyaniline, Detail Of Its Synthesis And Characterization.

Author[1]: Mohammadi Sadia Nausheen, Scholar at the department of Chemistry at Sri Satya Sai University of Technology and Medical Sciences, Sehore-MP.

Author[2]: Dr. Neelu Jain, Associate Professor at the department of Chemistry at Sri Satya Sai University of Technology and Medical Sciences, Sehore-MP.

Abstract: Synthesis of polyaniline as a main method to obtain conductive and electrically conductive composite materials. The conductive composite material is formed as a semiconductor. Organic polymer semiconductor materials such as polyaniline (polymeraldine salt) can be easily synthesized and it is the only conductive polymer material whose electronic structure and electrical properties can be reversibly controlled through the process. oxidation and protonation. PANI exists in three states: leucomeraldine, emerldin, pernigraniline. But only emerldine salt has conductive properties in semiconductor form. PANI has found use in many different applications, they can replace metals and semiconductors because they have conductive properties, low density and easy processability. Polyaniline is a representative of a family of conductive polymers with high environmental stability. This article presents a chemical method for synthesizing polyaniline and compares its semiconductor properties with conventional semiconductors.

Keywords: Synthesis, Polyaniline, Conducting Polymer, Analaysis, Semiconductor

1. INTRODUCTION

Polyaniline (PAN) is one of the most interesting conducting polymers due to its environmental stability (Qiu et. al 2005). The Polymer systems with unique properties are the recent fields of increasing scientific and technical interest, offering the opportunity to synthesize a broad variety of promising new materials, with a wide range of electrical, optical and magnetic property. Ease of synthesis and preparation [Saraswat, et. al. 2013] and wide-ranging potential use through its particular electrochemical, optical, and electrical properties. Technological uses depend crucially on the reproducible control of the molecular and super a molecular architecture of the macromolecular via a simple methodology of organic synthesis. Among the conducting polymer, Polyaniline (PANI) is one such polymer whose synthesis does not require any special equipment

or precautions. Conducting polymers generally show highly reversible redox behavior with a noticeable chemical memory and hence have been considered as prominent new materials for the fabrication of the devices like industrial sensors. The properties of conducting polymers depend strongly on the doping level, protonation level, ion size of dopant, and water content. Conducting PANI is prepared either by electrochemical oxidative polymerization or by the chemical oxidative polymerization method. The emeraldine base form of PANI is an electrical insulator consisting of two amine nitrogen atoms followed by two imine nitrogen atoms. PANI (emeraldine base) can be converted into a conducting form by two different doping processes: protonic acid doping and oxidative doping. Protonic acid doping of emeraldine base corresponds to the protonation of the imine nitrogen atoms in which there is no electron exchange. In oxidative doping, emeraldine salt is obtained from leucoemeraldine through electron exchanges. The mechanism causing the structural changes is mainly recognized to the presence of -NH group in the polymer backbone, whose protonati deprotonation will bring about a change in the electrical conductivity as well as in the color of the polymer.

2. MATERIALS

A. Conventional Semiconductor

1) Silicon: Silicon is a chemical element with symbol Si and atomic number 14. It is a hard and brittle crystalline solid with a blue- grey metallic lustre; and it is a tetravalent metalloid and semiconductor.

2) Germanium: Germanium is a chemical element with symbol Ge and atomic number 32. It is a lustrous, hard, grayish-white metalloid in the carbon group, chemically similar to its group neighbours silicon and tin. Pure germanium is a semiconductor with an appearance similar to elemental silicon.

3) ZnO: Zinc oxide is the inorganic wide band gap semiconductor compound and it is insoluble with water. Due to oxygen vacancies, it acts as N type semiconductor.It also act as piezoelectric material with PV application. As force is applied on ZnO, it develops internal polarization and develops voltage and current. It has ability to make thin flexible film. It can be used in PV, Piezoelectric sensor, acoustic micro sensor.

B. Conducting Polymer Material

We know that most of polymers are insulators and they can be used for insulating wires, cables, switches, measuring probes, tools and a variety of other items. In order to make them conductive we have to increase the carrier concentration. If one decreases the band gap and increase the delocalization of electrons then one may except higher conductivity in the materials. Polymers are generally offering a resistance of the order of giga ohm i.e. (10^9 ohms) and even higher than that consequently. The fact that polymers can be used as conductors of electricity and they can be made as good conductor as copper which is surprising. There are needs of lightweight materials which are conductive rather than metals like copper. Generally, metals have tendency of corrosion so that it diminishes (vanishes) after sometime. To overcome this difficulty a need can be completed by applying electrically conductive polymers. These electrically conductive

polymers can be used in potentiometers, different capacitors, PCBs as a transistors or a diode and in many other applications. Following are some conducting polymer material.

C. P3HT(3-Hexylthiphene-2, 5-diyl)

Regioregular poly(3-hexylthiophene) (P3HT) is used as a model polymer for research in organic solar cells. It is popular in spite of its dissimilarity in many respects to the high-performing class of polymers based on the donor–acceptor (DA) motif. Such as, P3HT has a low glass-transition temperature, is highly crystalline for a semiconducting polymer, is made by a living polymerization, and comprises no fused rings along the conjugated backbone; these characteristics stand in contrast to most DA polymers.

P3HT is the organic polymer material. It can be used for organic polymeric solar cell because of its small bandwidth. This material act as donor material, (P) type semiconducting material. P3HT is highly soluble, high thermal stability and excellent material for thin film. But disadvantage of this material is poor matching of photons absorbance with solar cell spectrum.

Sr. No.	Name of material	Property
1	P3HT	P Type semiconducting material
2	PCBM	N type semiconducting material
3	PANI	Act as P type, N type, piezoelectric according to doping
4	ZNO	Act as N type and piezoelectric

D. PCBM (Phenyl C61 Butyric acid Methyl Ester)

PCBM is the derivative of fullerene and it is organic polymer material. It has very good electron acceptor potential. So It may be used in polymer organic solar cell as acceptor, (N) type semiconducting material. It is excellent material for flexible thin film.

E. Conducting Polymer Materials

Table 1 .Conducting Polymer Materials

A. Electrochemical Synthesis

3. METHODS OF SYNTHESIS OF POLYANILINE

Amongst the all aforementioned four methods electrochemical process is the simplest method to achieve a suitable conducting polymer film. Hence this method is selected.

The method requires a monomer of which a polymer is to be prepared, suitable solvent in which a solute can be dissolved and some electrolyte for addition of conduction ions.

This can be taken in a beaker like container with suitable quantity two electrodes are used which are cathode and anode. Graphite used as a cathode electrode, at one end and steel plate at another end as an anode. This deposition requires very low voltage. A constant voltage power supply is generally preferred for the application of voltage to the cell so that constant voltage can be applied for the preparation of films of polymers. This voltage can be applied by two different methods. But in this project potentiostatic method is used.

a. Reaction

- Solvent + Monomer + Electrolyte Polymerization Conducting Polymer.
- Distilled Water + 1 M Distilled Aniline + Acid Polymerization Conducting Polymer.

B. Chemical Method

The chemical synthesis of polyaniline is effected by adding an oxidizing agent to the acidic solution of monomer under controlled conditions. Various chemical oxidizing agent such as potassium dichromate, ammonium persulphate, hydrogen peroxide, potassium periodate, ceric nitrate, potassium persulphate etc. have been used by different workers. Generally stoichiometric equivalent of oxidant is used since if used too high quantity of oxidant used degradation of the polymer is observed. The reaction is mainly carried out in acid medium particularly in Sulphuric acid medium at pH between 0 and 2. However, other acids such as HCl, HNO_3, H_2SO_4 maleic acid are also used (pH=1) as a medium of synthesis of polyaniline.

When chemical oxidant is added to aniline in a reaction vessel and left for a certain period of time under stirring, the solution gradually becomes coloured and greenish black precipitate appears. The colouration of the solvent is possibly due to the formation of soluble oligomers. The polymer synthesized by chemical method is then isolated from the reaction medium by filtration. The precipitate is then washed and conditioned using an appropriate solvent depending on the nature of the studies that has to be carried out. Further, free standing films can be obtained by dissolving the chemically synthesized product in a suitable solvent and casting it on a spin rotator. The processing of the films by such kind of method appears to be advisable since in many places these films are found to be suitable for certain applications.

C. Result

The peak observed at 3688 and 3544$cm^{-1}$is attributed to OH stretching vibrations. The characteristic bands at 3099 cm^{-1} is corresponding to Alkanes (-CH_2-) stretching CH Deformation.. The band around 3497cm^{-1} is attributed to the NH stretching. The bands around 1651& 1470 cm^{-1} can be assigned to CH medium and CH weak stretching. Thus the FTIR spectral results confirm the formation of Polyaniline.

D. Peak Analysis

Sr. No.	Peak No.	Wavelength Range	Bond strength	Group
1	1	3688	Medium	O-H Stretching
2	2	3544	Strong	O-H Stretching
3	3	3521		
4	4	3497	Medium	N-H Stretching
5	5	3200	Weak	O-H Stretching
6	6	3129		
7	7	099	Medium	C-H Stretching
8	8	2349	Strong	O=C=O Stretching
9	9	1651	Weak	C-H Bending
10	10	1470	Medium	C-H Bending
11	11	1300	Medium	O-H Bending

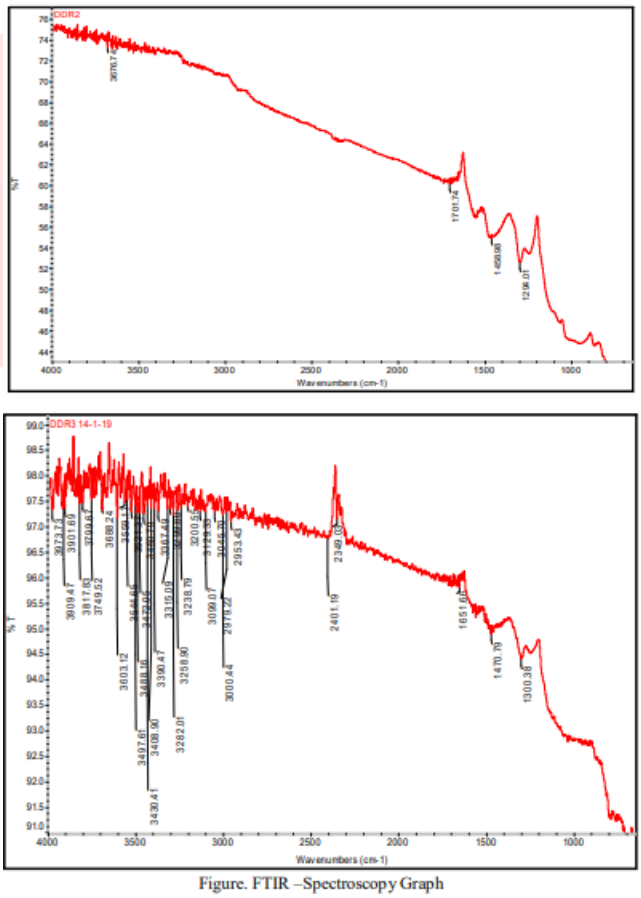

Figure. FTIR –Spectroscopy Graph

Figure. FTIR –Spectroscopy Graph

E. XRD(X-Ray diffraction)

X-Ray analysis is applied to the understanding of characteristics of nano-material and nanostructure of crystalline material, semi- crystalline materials and amorphous material. Analysis of peak shape give information about crystalline size and other aspect of microstructure.

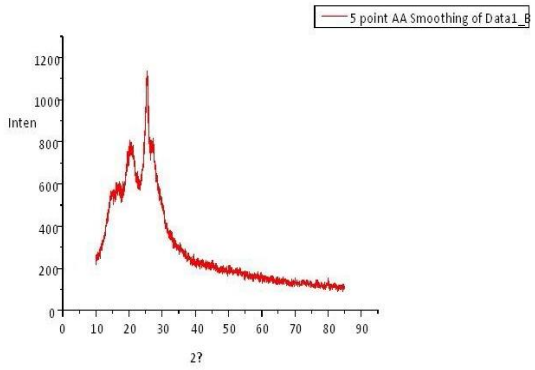

Figure. XRD Analysis Graph

From above graph its highest peak point has less dark so polyaniline shows crystalline material property. Crystalline material has higher conductivity than amorphous material.

Comparison with other semiconductor material

Sr.no	Comparison point	PANI	Si	Ge
1	Bandgap	1.9ev	1.14ev	0.67ev
2	Doping	HCl , H2SO4, PTSA, DBSA, LA	antimony, phosphorus, arsenic, boron, aluminium, gallium .	antimony, phosphorus, arsenic , boron, aluminium, gallium.
4	Structure	Flexible ,Crystalline	Crystalline amorphous, hard and brittle	Lustrous, hard
5	Flexibility	Flexible	Flexible at nanostructure	Flexible at nanostructure
6	Environmental friendly	Environmental friendly material	Less environmental friendly than PANI	Less environmental friendly than PANI
7	Colour	Green	Blue-gray	Grayish-white
8	Cost	Cheaper in cost	High cost	High cost
9	availability	Easily available in India	Not easily available in India	Not easily available in India

4. CONCLUSION

This paper shows the alternative method for synthesis of Polyaniline that can be used for the solar cell. Polyaniline is ranked among the most studied conducting polymers and It has the crystalline structure having the good semiconducting properties.

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