

Chapter 1

1.1 Overview:

Cutting-edge scientific and technological research in the area of novel composite materials boosts the development of new analytical tools. In this research work, we have tailored the properties of a composite system in order to get novel structures and improved properties for electrochemical sensor applications. This chapter deals with the basic introduction conducting polymers, polyaniline, and sensor/ biosensors, motivation, objective, and structure of this thesis.

1.2 Polymer:

Polymers are the chemical compound made up of many small repeated units- called monomer. It may be of one, two, or three-dimensional interconnected of chains. Bakelite is the first polymer to be manufactured in 1909. Rayon a derivative of cellulose was discovered in 1910. Nylon was first prepared in 1935. Organic polymers are composed of hydrocarbons, compounds of carbon and hydrogen but some other elements (oxygen, nitrogen, sulfur, chlorine, fluorine, phosphorous, and silicon. These polymers are specifically made of carbon atoms bonded together, one to the next, into long chains that are called the backbone of the polymer. Polymers have some general characteristics, chemical resistant, corrosion resistance thermal and electrical insulators, excellent surface finish, low-density, good strength, colored and transparent, heat sensitive, easy to process, poor tensile strength wide application range. The properties of polymers could be easily modified and enhanced by adopting different methods (Carragher et al. 2003; Ebewele et al. 2000).

Polymers could be classified in many ways, based on their source, structure, molecular force, and mode of polymerization (fig. 1.1). Based on the mechanism,

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polymerization is broadly classified as addition and condensation. In condensation polymerization smaller molecule (such as water, ammonia) released when two monomers combined together e.g. Nylon formed with monomers with carboxylic acids and basic amines. When monomers have unsaturation, they follow addition polymerization, which further categorized as free radical, cationic and anionic polymerization. Free radical polymerization follows fast kinetics. On the basis of cross-linking polymers are of two type thermostat and thermoplastic. Thermostat polymer deformed on heating because the three-dimensional network does not reform once melted e.g. adhesive made up of two epoxy resins. On the other hand, thermoplastic polymers have linear polymers (one-dimensional chains) with no cross-linking and it could easily melt, e.g. polyethylene. Polymeric materials have been used for a variety of advanced technological applications (fig 1.2) (Ghosh et al. 2006; Kumar et al. 2003; Ray et al. 1995; Das et al. 2012; Kumar et al. 2012; Shahadat et al. 2017; Ye et al. 2016; Mamaqani et al. 2012).

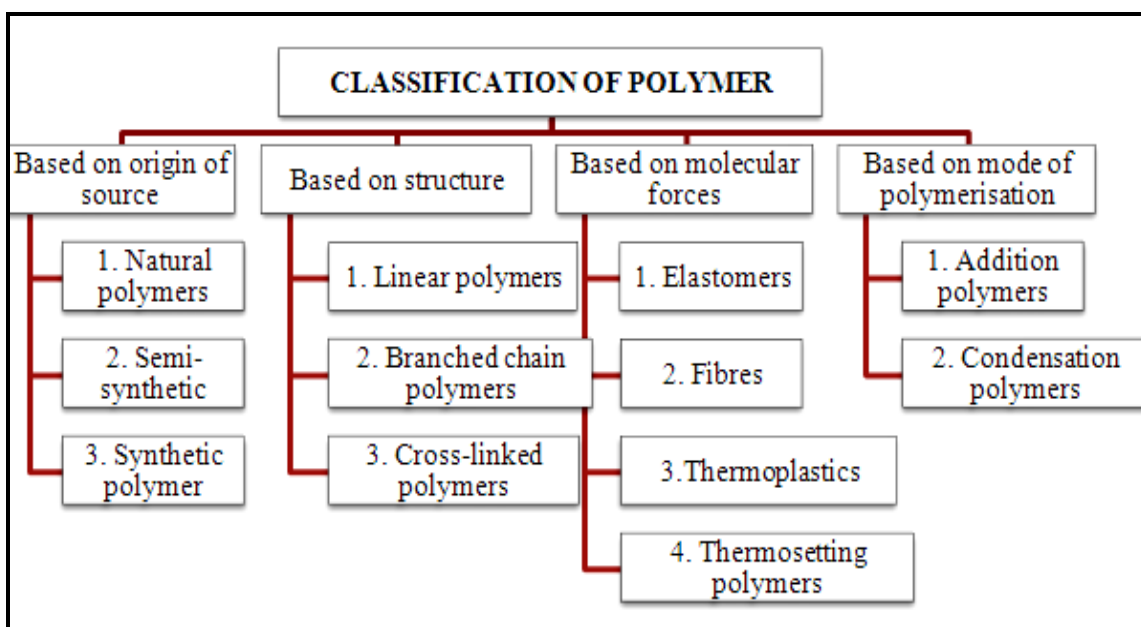


Fig. 1.1 Classifications of Polymers

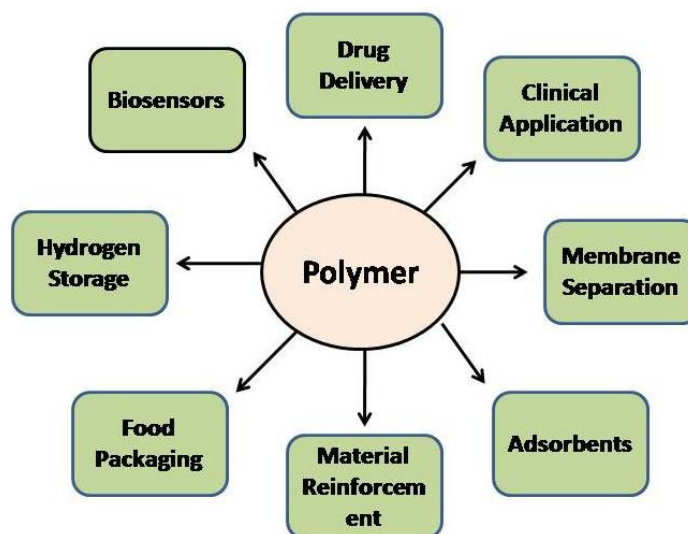


Fig. 1.2 Application of Polymer

1.3 Conducting Polymer:

Based on their electrical properties, materials are generally classified as insulators (10^{-7} S/cm), semiconductors (varies from 10^{-4} to 10 S/cm), conductors and superconductors (10^3 S/cm and more). Indeed, plastics are extensively used for its insulation property in electrical industry (Blythe et al. 2005). In 1962, John Pople and S.H. Walmsley predicted Conducting polymers, before their experimental discovery. They predicted the concept of “solitons” in polyacetylene and suggest defect could be mobile. In 1963, D.E. Weiss and coworkers reported iodine oxidized polypyrrole has high conductivity. In 1958, Natta and co-workers reported polyacetylene. Though the resulting material was highly crystalline and of regular structure, it was a black, air-sensitive, infusible and insoluble powder. In the early 1960s, Donald Weiss work on polypyrrole, and René Buvet and Marcel Jozefowicz on polyaniline. In 1862, H. Letheby analyzed the behaviors of the chemical reaction and study of

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electropolymerized aniline sulfate on a platinum electrode. In the early 1970s, inorganic explosive polymer, poly(sulphur nitride) $P(SN)_x$, was found to be superconductive at extremely low temperatures ($T_c=0.26$ K). The metallic character of $P(SN)_x$ is due to the presence of one unpaired electron. In 1974, Shirakawa and co-workers prepared a silvery film of polyacetylene (previously it was known as a black powder), using a Ziegler-Natta catalyst. In 1975, Professors Alan Heeger and Alan MacDiarmid studied metallic properties of $(SN)_x$. In 1977, Shirakawa, MacDiarmid and Heeger discovered halogen doped polyacetylene films is more conductive than the undoped state. In 1977 Gill *et al.* reported conductivity of PSN could be enhanced on exposing with bromine and similar oxidizing agents (Awuzie 2017; Hall et al. 2003; Huang et al 1986). The discovery of conductive polyacetylene motivates researchers to explore other conjugated polymers, such as polypyrrole, polythiophene, polythiophene, polyphenylenevinylene, polyaniline, and others. The properties of CPs could be improved by making a hybrid system with other material. Efforts are going on to develop novel materials having tailor-made properties for the desired application. Numbers of research papers published in the area of CPs has been increasing exponentially increase, shown in fig. 1.3.

On the basis of conduction mechanism, semiconducting polymers are of different types

(a) Extrinsic conducting polymer: This class of material has externally addition of some kind of conducting fillers. These are the conducting polymers whose conductivity is achieved by adding external ingredients to them. Various conductive fillers have been reinforced in polymers, as a result conducting polymer composites are obtained, e.g. metal powder/fiber, metal oxides, carbonaceous materials. The electrical conductivity depends upon the amount, distribution, and orientation of nanofillers.

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(b) Organometallic polymeric conductors: This class of material has organometallic groups in the polymer molecules. The d orbital of metal act as bridge between adjacent layer of polymer and it could overlap with an orbital of polymer chain, which leads to charge delocalization. The bridge transition metal complexes are stable and conducting systems without any external doping e.g. metallophthalocyanines, polyferrocenylene.

(c) Polymeric charge transfer complexes (Ionically conducting polymers): Polymer electrolytes or complex polymer are a new class of solid ionics. It exhibited low conductivity, depends on the humidity and they often nonconducting in the dry state. The ionic conduction mechanism requires the dissociation and migration of charge at different coordination sites. They are also called as ionomers, Nafion is a good example (Li et al. 2015).

(d) Inherently/intrinsic conducting polymers (ICPs): It is a class of polymers which shows electrical conductivity without using any conductive additives. Conjugated structure (alternating single and double bonds), and the π electron delocalization along their polymer backbone is the source of conductivity for this type of polymers.

Conducting polymers is an interesting class of polymeric materials and attractive area of research. It has a combination of properties of organic polymers and semiconductors/metals. Conjugated polymer generally needs some kind dopant (redox or nonredox dopants) which improves the conductivity to a great extent. It can be further categorized into two groups - conducting polymers have conjugation; doped conducting polymers. Some examples of intrinsic conducting polymers are given in fig. 1.4. CPs could be easily oxidized or reduced than conventional polymers because they have lower energy optical transition, lower ionization potential, and high electron affinity. CPs shows a wide range of conductivity from metal to insulator (fig. 1.5). CPs have following important

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characteristics low hydrogen content and aromatic structure, reversible doping/dedoping process, high surface area, electrochemical activity, higher conductivity, lower manufacturing costs, better processability, low density, high mechanical flexibility and tunable properties. Its properties greatly depend on doping level, protonation level, charge and size of dopant, water content, chain orientation, conjugation length, intra- and inter-chain interactions and purity of the sample. Due to the restricted rotation of groups, these polymers exhibited high melting points and could not process through molding. Their unusual properties of conducting polymers open new fascinating direction of intelligent, smart, functional nanomaterials. Investigation of structure relationships with electrical, optical, electroluminescence and other physical properties is the current trend conjugated polymers research, in order to explore its application in following technological applications, such as printed electronic, molecular electronics, supercapacitors, electrochromic displays, chemical sensors, light emitting-diodes, actuators, electromagnetic shielding, organic photovoltaic devices, field effect transistors and non-linear optics (Yang et al. 2017; Mude et al. 2017; Das et al. 2012; Le at al. 2017; Li et al. 2015; Bakhsi et al. 2004; Prasanna,et al. 1991; Skotheim et al. 1997; Gyorgy et al. 2012)).

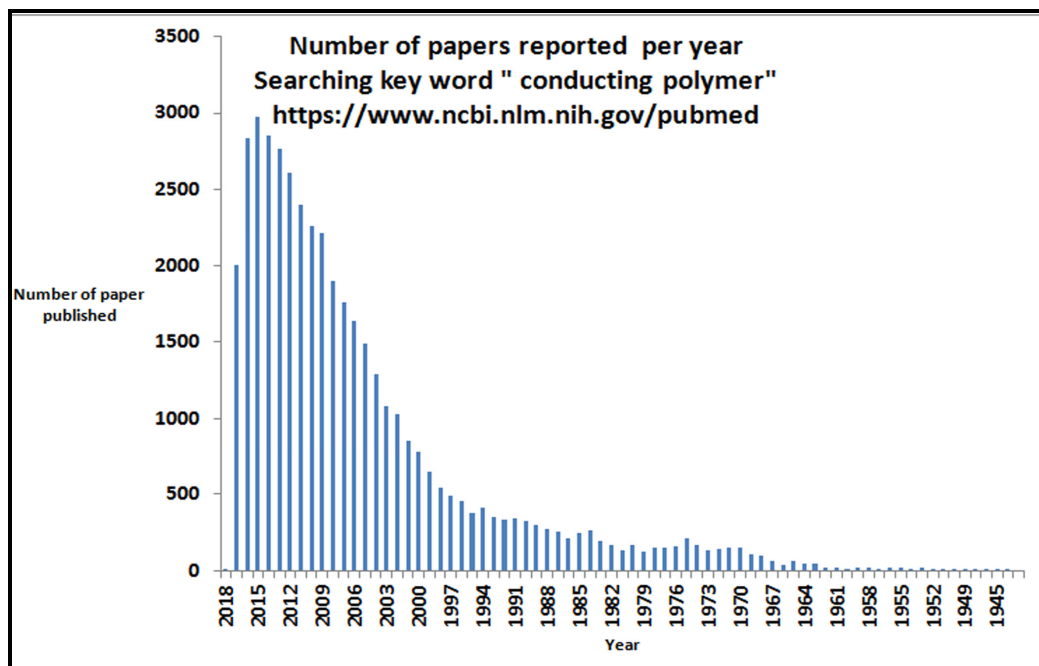


Fig. 1.3 Number of research papers published on conducting polymers (Source: Pubmed)

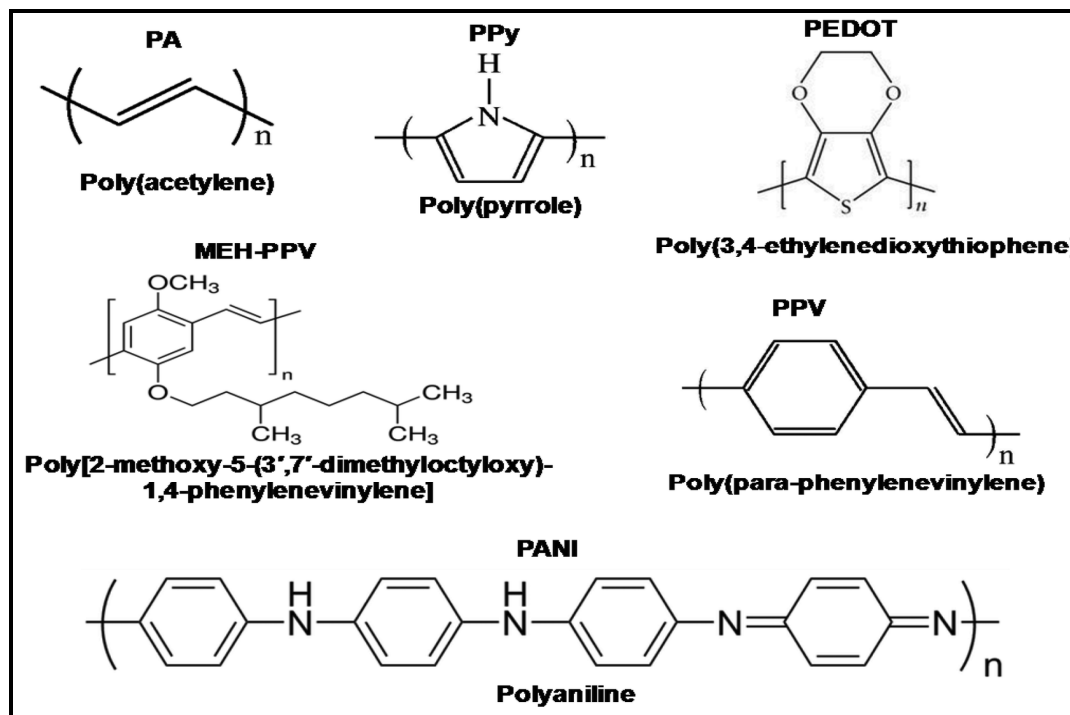


Fig. 1.4 Selected examples of intrinsic conducting polymers

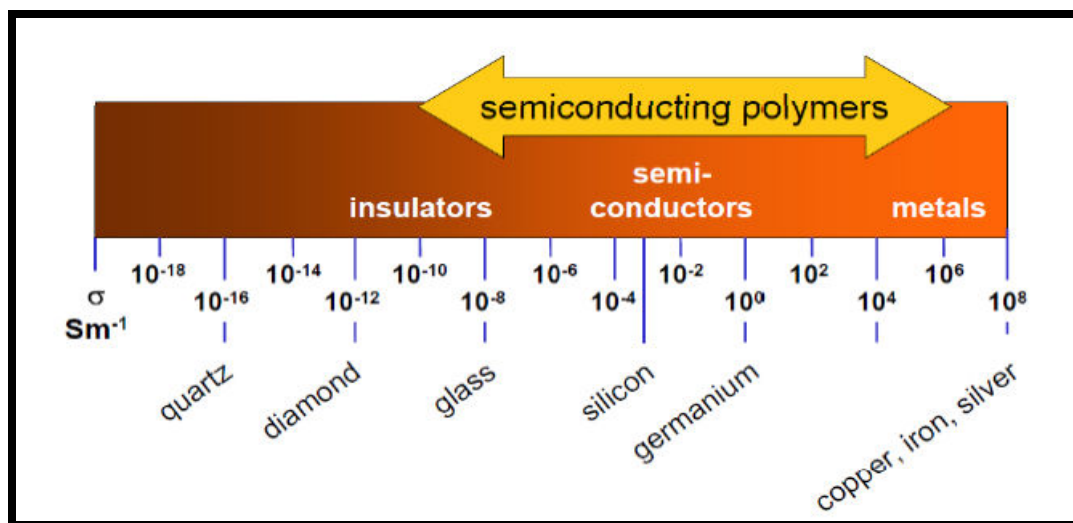


Fig. 1.5 Conductivity ranges of materials

1.3.1 Synthesis of Conducting Polymers:

Various methods have been reported for the synthesis of conducting polymers can be synthesized by any of the following methods; chemical, electrochemical, photochemical, metathesis, concentrated emulsion, inclusion, solid state, plasma polymerization and pyrolysis (Awuzie 2017). ICPs are commonly formed by using either chemical or electrochemical methods. In the free radical oxidative chemical polymerization coupling takes place by using chemical oxidants at a specific temperature. The monomer is first oxidized using some kind of oxidizing agent, into a radical cation. The two radical cations coupled together as a dimer which further propagates to join with other dimers and finally produces oligomers and polymers. Pure conducting polymers obtained after appropriate washing and drying. In the electrochemical polymerization, radical cations generated at the initial step via an applied potential using electrolyte solution containing monomer and

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dopant. A three/two electrode system could be used (Janta et al. 2003; Bredas et al. 1985; Ghosh et al.2006; Kumar et al. 2003).

1.3.2 Conduction Mechanism of Intrinsic Conducting Polymer:

On the basis of the band theory, materials could be classified in three categories (metal, semiconductor, and insulator). Electrons could move within discrete energy states called bands and the gap between valence band and conduction band called energy band gap. The band gap band determines the relative ease with which electrons will jump across the gap and electrical properties of the material. If the band gap is small (e.g., 2.0 eV), the valence electrons can be excited into the conduction band by thermal or phonon excitation. The electrons then become mobile, and the material is termed a semiconductor. By analogy, the bonding and antibonding hybridized π -orbitals of conducting polymers generate energy bands fully occupied π -band are valence band and empty π^* -band conduction band (fig. 1.6).

The π -conjugated polymers have a continuous array of overlapping π -orbitals. These π structures in conjugated polymers are highly prone to oxidation or reduction due to low ionization energy and high electron affinity. The unpaired π electron per carbon atom in the conjugated polymers is only loosely bound and have restricted span of movement. Doping creates charge carriers can be formed in the polymer chain, where holes and electrons move in opposite directions. The removal of electrons creates polaron and bipolaron (a bipolaron is a bound pair of two polarons). If one electron removes polaron obtained, with the successive removal of another electron, bipolaron can be generated. When a bipolaron structure is generated, they can readily separate (known as a soliton). Highly doped CPs has an additional defective band between valence band and conducting band. These quasi-particles

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facilitate the overlapping of orbitals and delocalization of charge, and the polaron and bipolaron states exist at mid gap. The relative concentration of the charge carriers/self-localized excitations (solitons polarons, and bipolarons) determines the electrical conductivity in conjugated polymers (Bredas et al. 1985; Ravichandran et al. 2010; Hand and Nelson, 1978; Genies et al. 1985; Kuzmany and Sariciftci et al. 1987; Travers et al. 1988).

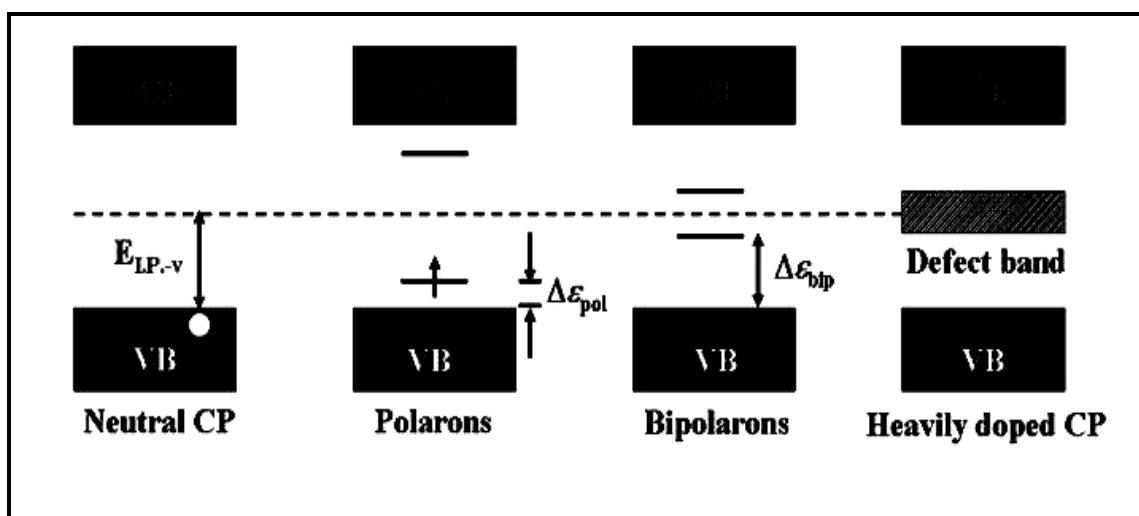


Fig. 1.6 Electronic band structure of conducting polymer without and with defect state

ICP have low conductivity in pristine form, but their conductivity can be improved by the technique called doping. A dopant's role is either the removal or the addition of electrons/holes in the material. Heavily doped conducting polymer has an intermediate band between valence and conduction band (fig. 1.6). Dopants can be classified as neutral dopants, ionic dopants, organic dopants, polymeric dopants. Dopant does not replace any atom from the polymer chain but they placed in between the polymer matrix. Dopants either oxidize to create a positive charge or reduce to create a negative charge on the chain, where oxidation

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and reduction of the dopant create positive/ negative charge on the polymer chain. Dopant facilitates the transition of charge from highest occupied orbital to lowest unoccupied orbital. To maintain the charge neutrality, counter ions inserted in the polymer matrix from the supporting electrolyte (MacDiarmid et al. 1985).

Neutral dopant	Ionic dopant	Organic dopant	Polymeric dopant
I ₂	LiClO ₄ ,	CF ₃ COOH,	PVS
Br ₂	FeCl ₄ ,	CF ₃ SO ₃ Na,	PPS
AsF ₂	CF ₃ SO ₃ Na	p-CH ₃ C ₆ H ₄ SO ₃ H	PAA

A redox dopant promotes the extraction of charge from HOMO in oxidation doping and or to the LUMO on reduction doping. To maintain the electro-neutrality of the polymer chain, this addition or removal of charge is compensated by the insertion /extraction of the counter ions supporting electrolyte. A charge could be injected into the polymer matrix by any of the following method; electrochemical, chemical, metal-polymer interaction, and photochemical. A non-redox dopant only brings a change in the energy level without any change in the number of electrons, e.g. protonic doping of polyaniline emeraldine base with aqueous protonic acids, such as HCl (Wise et al. 1998; Saxena et al. 2002).

Bulk conductivity of a material depends on the density of charge carriers and their mobility, but intermolecular charge transfer reaction could be limited due to bad contacts between different crystalline domains. Better conductivity observed for the well ordered and closely packed structure is attributed to better interchain charge transfer. Disorder, inter/intra

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chain interaction and doping level determines the insulator-metal transition in conducting polymers. Figure 1.7 shows inter, intrachain and intradomain charge transfer.

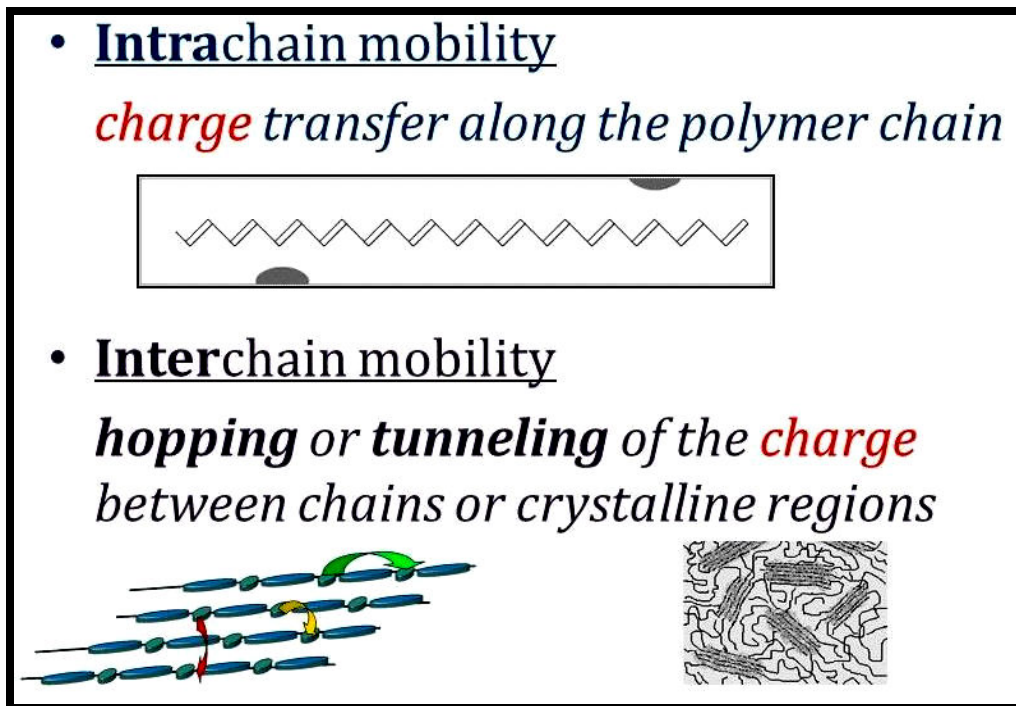


Fig. 1.7 Inter, intrachain charge transfer and interdomain transportations

1.4 Polyaniline (PANI):

Polyaniline is the oldest and most studied conducting polymer. The interest in polyaniline has increased significantly due to its low cost, facile synthesis and easy doping/dedoping, interesting electrical, electrochemical, electrochromic, and optical properties. It does not dissolve in common solvents and does not diffuse during melting. Many researchers found that polyaniline doped with organic dopant could be dissolved in organic solvents. The discovery of polyaniline was begun with the initial oxidation of aniline by F. Ferdinand Runge in 1834. It was studied and used for the variety of colored materials and dyes. PANI was first known in 1835 as “aniline black” a term used for any product under acidic condition

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obtained by the oxidation of aniline. In 1862, Henry Letheby reported for the first time the electrochemical oxidation of aniline, but unfortunately, the electrical properties were not measured at that time. Polyaniline discovered in the early 1860s by Lightfoot. Polyaniline based materials have been used for a variety of technological applications as extensively reported in the literature (Ghosh et al. 2006; Kumar et al. 2003). Numbers of research and review articles have been increasing exponentially since last two decades (fig. 1.8).

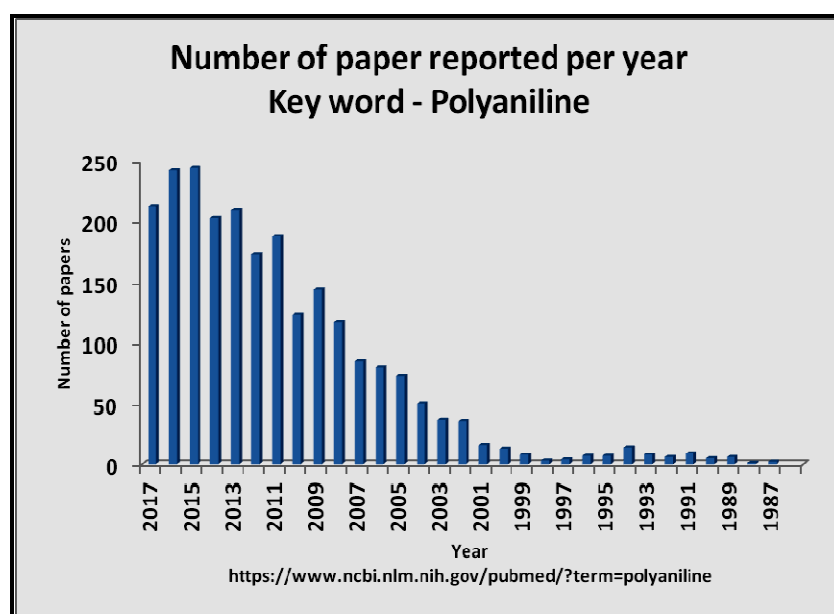


Fig. 1.8 Number of research papers reported on Polyaniline (Source: PubMed)

1.4.1 Chemical Structure and Morphology of PANI:

PANI is a p-type semiconducting polymer and it contains benzenoid, quinoid rings and nitrogen atoms. The nitrogen atoms may be of imine or amine form. On the basis of relative composition two states of nitrogen and quaternized state or not, it exists in three distinguish, isolable oxidation states, in its base and salt form

(a) Leucoemeraldine: the fully reduced form.

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(b) Pernigraniline: the fully oxidized form.

(c) Emeraldine: the partial oxidized (the ratio $-N^-/-N^=$ is 0.5).

Polyaniline has variable oxidation state and the degree of oxidation can be of any value in 0-100 scale. In doping condition, the base form of polyaniline converts into salt form. Emeraldine salt is the only conducting form of polyaniline. The chemical structure of polyaniline depends upon the level of protonation and level of oxidation. The structural change of polyaniline corresponds to the change of pH and redox potential. Electrical conductivity and colour of polyaniline depend on the protonation/deprotonation equilibrium. Protonic acid doping convert emeraldine base to emeraldine salt (insulator-to conductor transition) without a change in the number of π -electrons. In oxidative doping, leucoemeraldine convert into emeraldine salt with electron exchanges. When PANI is doped with an acid, polaron and bipolaron structures participate in the electrical conduction. In polaron structure, the positive charge on nitrogen act like a hole and nearby nitrogen electron jumps into this hole to neutralize it. As a result, charge mobile along the polymer chain. On the other hand, such movement not possible in bipolaron structure because two holes are adjacent to each other. Primary, secondary and tertiary structure is a linear arrangement of benzenoid and quinoid units, compact coils structures and amorphous architecture, respectively.

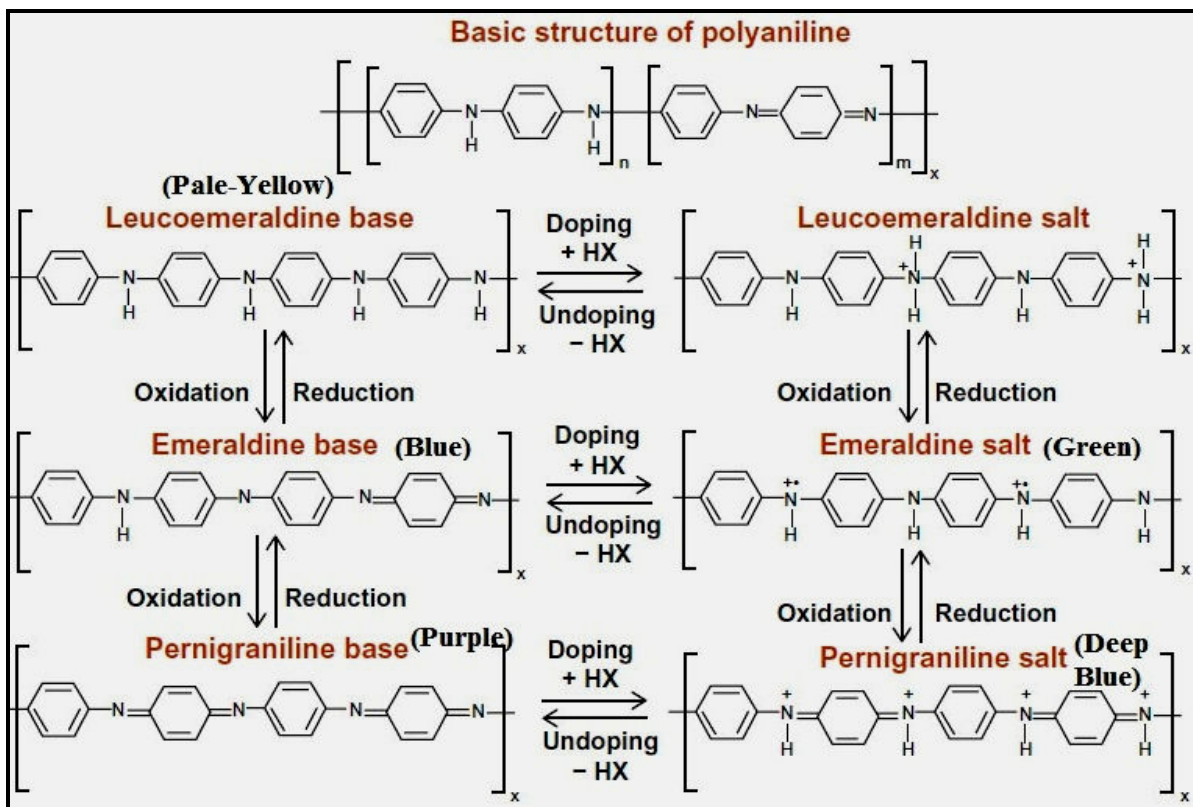


Fig. 1.9 Structures of different forms of Polyaniline (Dhand et al. 2015)

The morphology of polyaniline depends upon various factors. Scientists have explored how various experimental parameters impact on the morphologies and the specific shape nanostructures have been developed (such as nanotubes, nanofibers, globular, nanoflakes, nanorods, nanospheres, core-shell structure) by using different methods (such as electrospinning, interfacial polymerization, rapid-mixing, nanofiber seeding, soft and hard template-assisted synthesis, and surfactants, or oligomer-assisted polymerization). In the different initial pH of the reaction mixture, the different proportion of anilinium ion and neutral aniline molecules leads to different PANI nanostructure under different nucleation

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mechanisms (Shi et al. 2013). Nanostructures of PANI exhibited superior properties than bulk/irregular shape PANI, due to their high surface area-to-volume ratio.

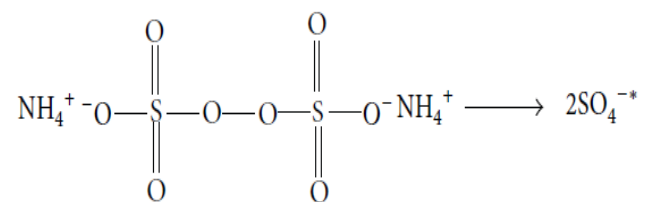
1.4.2 Synthesis of Polyaniline:

The synthesis of Polyaniline does not require any special equipment or safety measures. The mechanism of polymerization is well reported in the literature. Most commonly, polyaniline prepared by chemical or electrochemical oxidations of aniline in a protonic acid. At initial growth stages, linear chains are formed. The level of nucleation, mechanism of polymerization greatly impact on the nanostructure and molecular weight of the polyaniline. Linear microfibrils produced in the early phase of polymerization, which coupled with other monomers and irregular shape particle developed in secondary growth (due to agglomeration of the linear chains). For large scale production, the chemical method is more convenient, whereas electrochemical method provides better opportunity to control reaction, however, have lower yield. PANI Film could easily be obtained by electrochemical route. The synthesis method and processing conditions (nature of acid and associated anionic dopant, reactant concentrations, reaction time, stirring, choice of oxidising agent and ratio of amounts of oxidising agent and monomer, pH, temperature, emulsifying/doping agent concentration and presence of additive/templates) play an important role in tailoring polymer properties. With the increase in polymerization duration and the decrease in polymerization temperature, the yield and the conductivity of polyaniline increase. The mechanism of polyaniline formation is well reported in the literature: radical formation (scheme 1), dimer formation (scheme 2) and polymer formation (scheme-3). In general, free radical polymerization follows three general steps- nucleation, propagation (initial growth, and secondary growth)

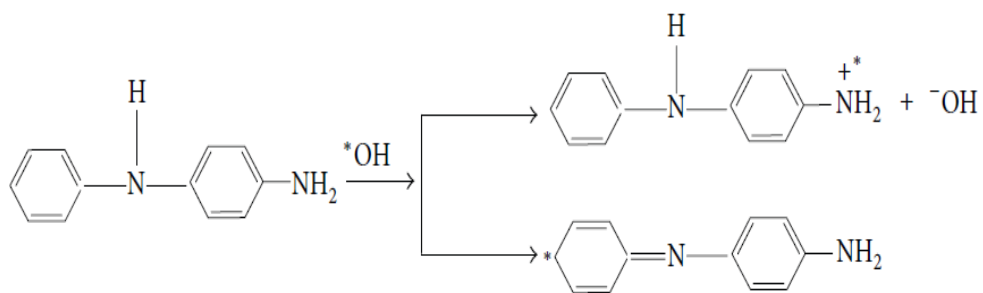
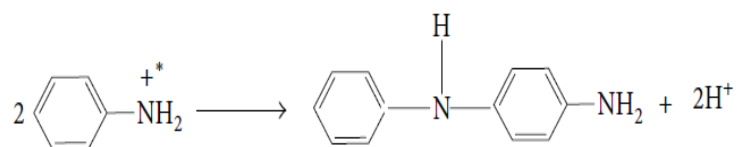
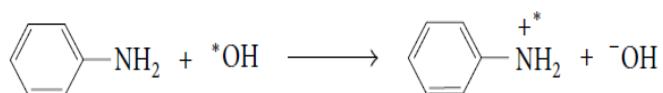
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and termination. Aniline monomer oxidized (by oxidizing agent/electrode process) to anilinium radical cations which coupled with another monomer and gives a dimer radical cation and on continuation of the reaction the chain start propagates and leads to the oligomers/polymer formation. Chain propagation continues until the chain terminated. After complete polymerization, the green colour emeraldine salt obtained.

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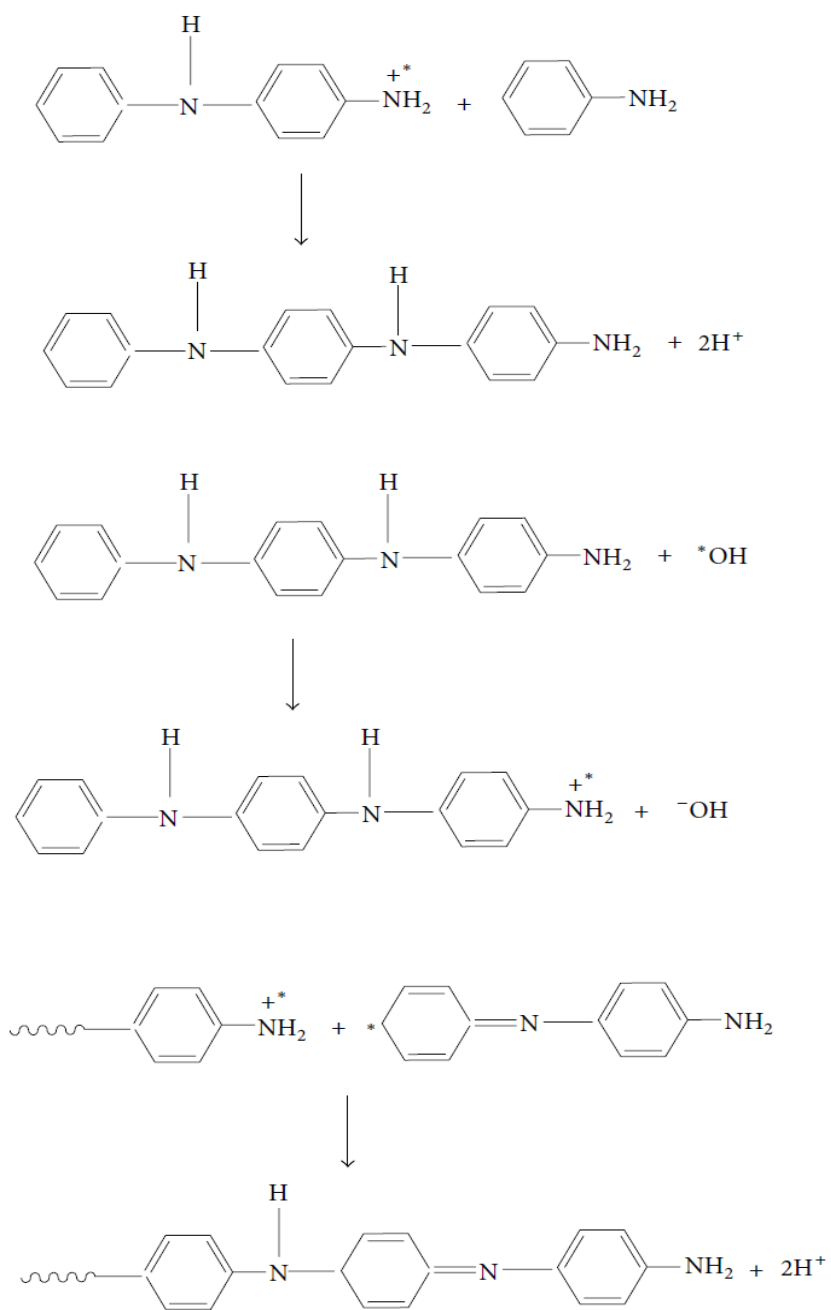


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1.4.3 Electrochemical Properties of Polyaniline:

PANI exists in variable oxidation states. Electroactivity of polyaniline could be easily explain the on the basis of conversion of one oxidizing state to another. Voltammetry is a common method to investigate the electrochemical activity of PANI. Cyclic voltammetry reveals two redox processes corresponding to the transitions from leucoemeraldine to emeraldine and from emeraldine to pernigraniline. The electroactivity of PANI greatly depends on the pH of the medium and it could be evaluated by measuring the peak current and peak position in the voltammetric studies (details on the electrochemistry of polyaniline have been extensively discussed in the successive chapters).

1.5 Nanocomposite Materials:

Composite materials are extensively observed in nature e.g. bone, wood and etc. A composite material can be defined as an arrangement of two or more materials whose properties are superior to those of the constituent materials acting independently. Composite synthesis provides an opportunity to overcome the individual deficiency of a material. Properties of the composite are strongly dependent on the nature of its constituents, distribution, interaction and the geometry and distribution of the reinforced particles. Properties of the composite system could be easily tailored on the basis of the requirement for any desired application. Generally, a composite system has two phases: reinforcing phase (discontinuous phase) and matrix (continuous phase). The reinforcing phase may be in form of particles, flakes or fibers (short or continuous long fibers). Matrix materials used in composites are typically ceramics, metals, and polymers.

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Cutting-edge scientific and technological research on materials has opened new directions for many applications. Globally, nanotechnology is an interesting area of research, many research groups have been working on the various type of nanomaterials for diverse applications. “Nanomaterials describe, in principle, materials of which a single unit is sized (in at least one dimension) between 1 to 1000 nanometres (10^{-9} meter) but usually is 1 to 100 nm” (<https://en.wikipedia.org/wiki/Nanomaterials>). Nanomaterial exhibited very distinct properties than atomic and bulk forms due to large surface area and high aspect ratio, properties of a nanomaterial is size and shape dependent. Many advanced nanocomposite materials have been used for a variety of technical and engineering applications. “Nanocomposite is a multiphase solid material where one of the phases has one, two or three dimensions of less than 100 nm” (<https://en.wikipedia.org/wiki/Nanocomposite>). Functionalized nanomaterials have received great attention in nanoscience and nanotechnology. Nanocomposite can be classified as ceramic matrix nanocomposites, metal matrix nanocomposites, and polymer matrix nanocomposite. A small amount of reinforcement of nanoparticles significant changes in the macroscale properties of the composite). Concentration, orientation, and distribution of nanoparticles are important factors which decide the properties of composite system.

1.6 Polyaniline Based Composite Materials:

Polyaniline based composite materials have improved properties than pristine polyaniline in term of better processability, conductivity, electroactivity, stability, solubility and specific shape micro/nanomorphology. Such improved and unique properties open horizons for many new applications. Polyaniline based composites have been prepared by different methods i.e.

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in-situ/ ex-situ chemical polymerization, in-situ electropolymerization, emulsion polymerization, interfacial polymerization, solution mixing, casting, layer by layer deposition, solid state synthesis, melt mixing, mill mixing, self-assembly, solution/dispersion mixing, and thermal reflux. PANI could easily interact with other material and chemical compound because it is polar and have hydrogen-bonds and porous morphology).

Material selection has great importance in the development of an analytical device. Nanomaterial-based electrochemical sensors exhibited better analytical performances due to excellent catalytic activity, conductivity and biocompatibility, stable bioconjugate, signal enhancement, high surface-to-volume ratio and good catalytic activity (extensively discussed in chapter 2)

1.7 Sensor:

The most familiar sensors in the human body are those that relate to vision, hearing, taste, smell and feel. The terms ‘sensor’ and ‘transducer’ have frequently been usually used as synonyms. The word sensor is obtained from the Latin word “sentire” which means ‘to perceive’. The American National Standards Institute (ANSI) standard MC 6.1 defines a transducer as ‘a device which gives a usable output in response to a specific measured’ (Instrument Society of America, 1975). A sensing device, sensor, detected the presence of physical properties and/or measure the change in physical quantities, and then converted them into signals comprehensible by a person or instrument.

Sensors can be classified on the basis of the type of recognizing element (chemical / biological), mode of transduction (piezoelectric, optical, thermal, ion-sensitive FET, electrochemical) and interaction of analyte with sensing element (affinity sensor and catalytic

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sensor). Biosensors could be considered as a subclass of chemical sensor is the device which used biological element for recognition and sensitive detection. Figure 1.10 shows the block diagram of a typical biosensor. On the basis of biological element biosensors are classified as; enzyme electrode, immunosensor, DNA sensor, microbial sensor, respectively. Based on the parameter to be measured, the electrochemical sensors are three type's conductometric, amperometric, potentiometric, impedimetric. Figure 1.11 summarized the different ways for the classification of biosensors. The field of the biosensor technology is a booming area of research throughout the world. There is an exponential increase in the number of research papers (on sensors) published per year, shown in fig. 1.12. Researchers are exploring novel materials and protocols to develop biosensors for real-time applications to detect a variety of analytes (Thevenot et al. 1999; Buerk et al. 1990).

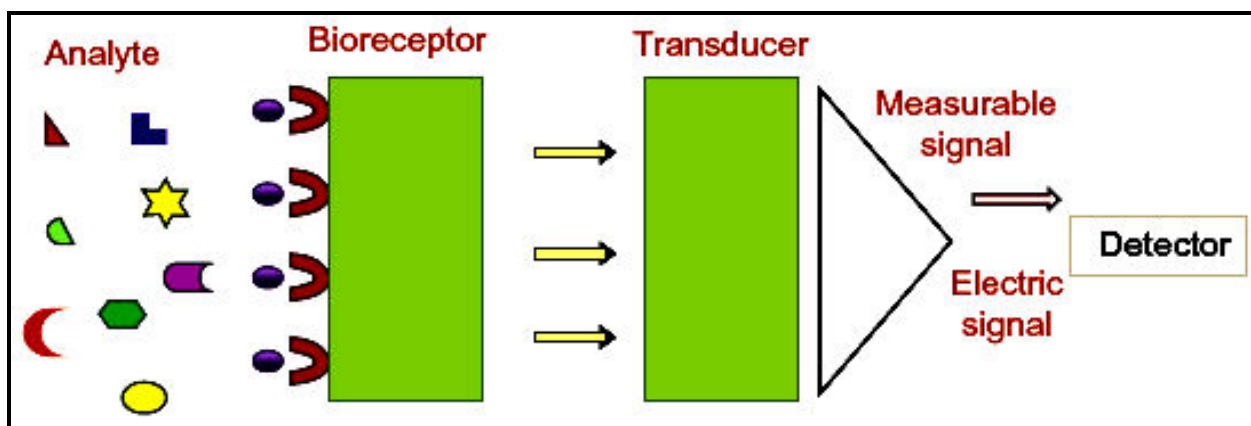


Fig. 1.10 A typical representation of a biosensor (Kumar et. al. 2016)

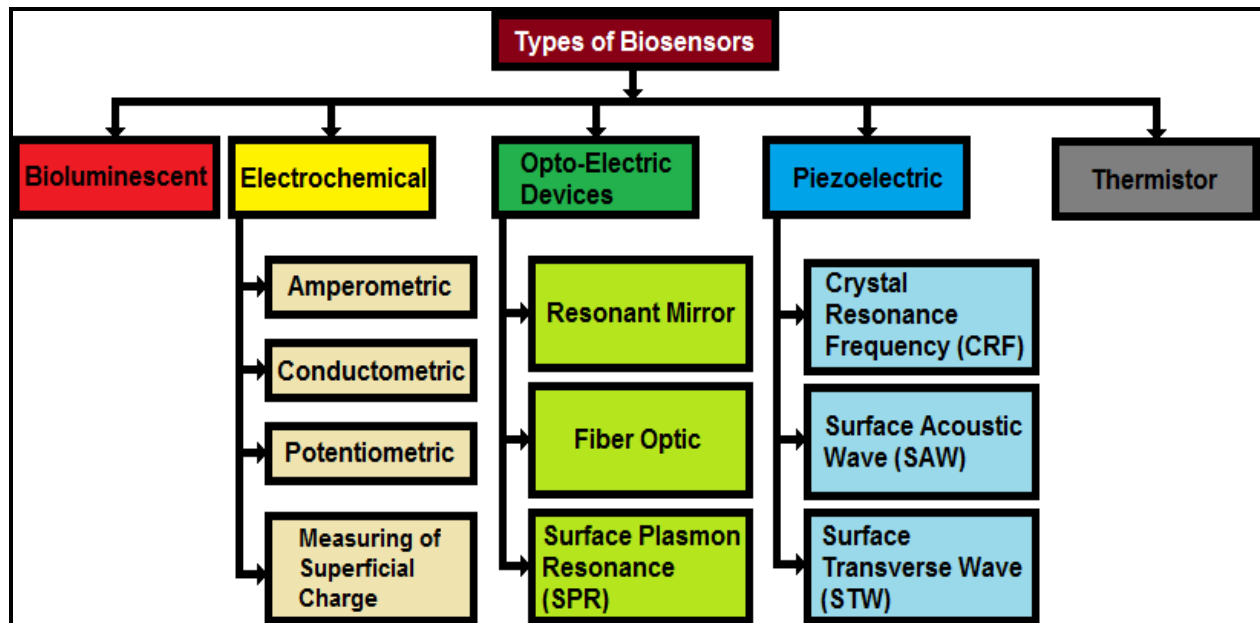


Fig. 1.11 Classification of biosensors

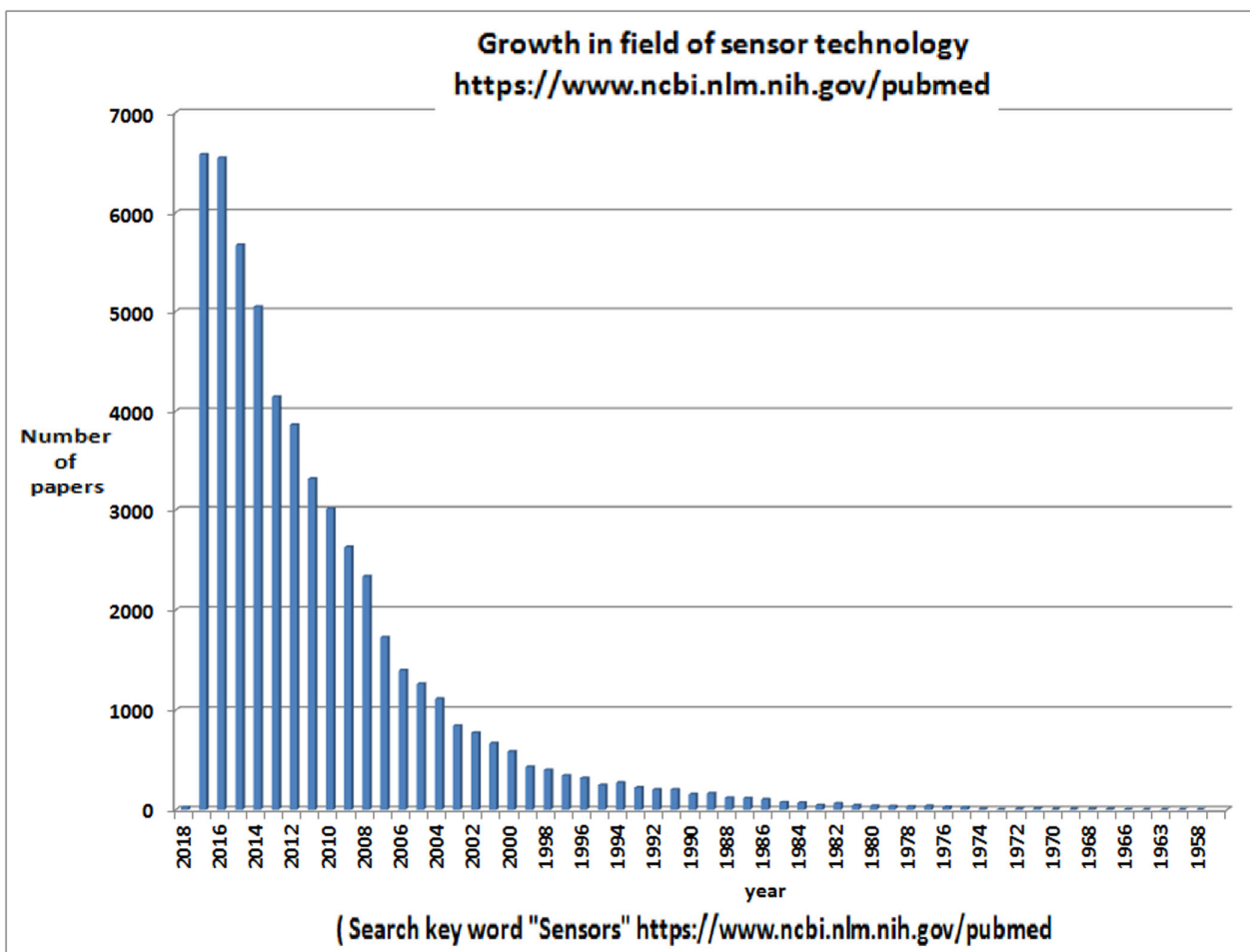


Fig. 1.12 Number of research papers published on sensor (Source: PubMed)

Electrochemical Sensor:

In the electrochemical sensor, a working electrode is the transducer element where the specific biochemical reaction takes place. Generally, three electrodes are used in such a system, voltage applied between the reference and working electrode, and current measured between working and counter electrode. Working electrode is also called as sensing/redox electrode, Ag/AgCl or Hg/HgCl₂ is two commonly used reference electrode, it maintains a

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known and stable potential. No current flow through reference electrode. A long platinum wire is used as a counter electrode and it carry current to/fro from working electrode. The redox reactions produce current or the potential difference at the working electrode, which utilize to quantify the amount of an analyte. The as a result of the oxidation and reduction reactions involving the analyte are used for its quantification in the sample. They have more stable output, have high sensitivity, fast response and suffer from lesser interferences. The various electrochemical parameters that could be monitored are current, potential, charge and impedance. In 1962 Professor LC Clark proposed the first biosensor, in which a oxygen electrode is entrapped in a thin layer of glucose oxidase (GOx) via a semipermeable dialysis membrane was used to detect oxygen consumption by the enzyme-catalyzed reaction (Nelson et al. 2003; Janata et al. 2003). Biosensors have many applications in food, environmental monitoring, clinical diagnoses, study of biomolecules and their response, drug development, crime detection, quality control, industry process control, and biodefense due to their selectivity, sensitivity, stability, and quick response time (Higgins et al.1987, Hulanickia et al. 1991, Ghindilis et al.1997).

a. Potentiometric Sensor:

The Potentiometric sensor measures the electrical potential difference between a working (potential changed during measurement) and the reference electrode (constant potential during measurement). Potentiometric sensor used to monitor charge accumulation, at zero current, on the selective affinity of analyte at the working electrode. The electrode may be selective for certain ions or gases and these include F^- , I^- , CN^- , Na^+ , K^+ , Ca^{2+} , H^+ , NH_4^+ , CO_2 , NH_3 etc. Potentiometric measurement or ion-selective electrodes are based on the difference

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in activity of the target analyte in two solutions typically separated by a glass membrane. First attributed to Cremer in 1906, the most widely used example of the ion-sensitive electrode is in the detection of pH levels.

b. Conductometric Sensor:

This class of sensors based on the measurement the variation in the electric conductivity due to the analyte. The conductivity of electrode material or solution varies with the associated redox reaction at the working electrode. Generally, such sensors are of low cost, and simple fabrication (no need of any reference electrode). Selectivity can be improved by modifying the electrode surface. Example of some conductometric sensors are - oxygen sensor, humidity sensor, ammonia sensor, hydrogen sulphide sensor, methane sensor (Smyntyna et al. 1995; Qu et al. 1997; Meekawa et al. 1994; Rumyantseva et al.1996; Devi et al. 1995). Resistance measured from a DC current is typical. Often the measurement is done with AC current (impedance), which also allows one to obtain changes in capacitive impedance.

c. Impedance Sensor:

In an impedance based sensor a sinusoidal signal of small peak-to-peak current is sent through an electrode. The change in the sinusoidal response is compared to the original and conclusions are made based on the type of change. Typically, several frequencies over a range of hundreds to thousands of kHz are chosen so that a comparison can be obtained. Selection of the minimum and maximum frequency is made based on the rate of sampling desired and the rate of change expected by the system. Faradaic processes, concentration

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polarization, and double layer charging diminish by using AC voltage. Some examples of impedance sensor are NO₂ and tobacco smoke, odor detection (Souto et al. 1996; Akiyama et al. 1996; Daniels et al. 2007).

d. Amperometric Measurements:

Amperometric detection involves the measurement of the current generated at a constant applied potential. The current generated is proportional to the amount of electroactive analyte. Electroactive analyte electrocatalytically oxidized at the electrode surface, the sensitivity and selectivity of the electrode reaction improved immobilizing suitable catalyst at electrode surface (biocatalyst in case of biosensor). Transfer of charge is an essential operational feature of voltammetric or amperometric devices. It is the most common commercial sensors accessible nowadays due to their low cost, rapid response time and higher sensitivity, precision, and accuracy compared to potentiometric sensors. Amperometric biosensor may be classified in three generations based on mode of charge transfer from enzyme to electrode surface: first generation biosensor, second generation biosensor, third generation biosensor. A two/three electrode system is required to fabricate an amperometric sensor using appropriate electrolyte solution. The surface of the working electrode modified in order to improve the sensitivity, selectivity of the sensor. Ag/AgCl and Hg/Hg₂Cl₂ is the two commonly used reference electrode which provides a stable voltage to the working electrode and no current flow through a reference electrode. Platinum/ graphite are generally used as a counter electrode to carry current. A supporting electrolyte eliminates the electromigration effects, lower the solution resistance and provide constant ionic strength (Stradiotto et al. 2003).

1.8 Road Map of the Work Plan and Dissertation Outline:

1.8.1 Motivation and Objectives:

Polyaniline based materials offer excellent platforms for electronic or optical signal transduction, improved analytical performance of bioelectronic and biosensing devices. In this thesis combines fundamental studies on the polyaniline/polysaccharide composite material, with deep application-driven studies for electrochemical sensor. Interesting properties of Polyaniline based materials motivated us to explore and compare important characteristics hybrid materials of polyaniline/polysaccharides material systems. Carbohydrates are nonconducting nonelectroactive, biocompatible, environmental friendly material. Numerous hydroxyl groups and bonded water molecules promote the formation a network of hydrogen bonds which facilitate the dispersion of the material in aqueous solution. Carbonaceous nanomaterial improves the strength, electrical conductivity and catalytic properties.

The main objectives of the present thesis are

1. Develop novel nanocomposite materials for sensor/biosensor devices.
2. To prepare the novel PANI and polysaccharide composite systems and explored structural, morphological, electrical, thermal, spectroscopic, and electrochemical characteristics using instrumental techniques.
3. Explore the application on developed composite materials for electrochemical sensor.
4. Optimized and compared the sensor performance.

1.8.2 Structure of the Thesis:

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This thesis deals with the synthesis, characterization and application of novel PANI based nanocomposite materials. It has been organized in nine chapters and associated additional data are included as appendix.

Chapter 1 gives general introduction of conducting polymers, polyaniline and sensors.

Chapter 2 presents a brief literature review about the polyaniline based composite materials and their application on electrochemical sensors.

Chapter 3 presents the brief description on the different analytical techniques and general experimental procedure for the preparation and techniques used to investigate morphological, optical, structural, thermal, electrical, and electrochemical characteristics of material prepared; SEM, TEM, HRSEM, FTIR, UV-Visible, Raman, XRD, TGA, DTA, DSC, CV, chronoamperometry and chronocoulometry.

Chapter 4 deals with the comparative study on PANI/Polysaccharide materials using starch, carboxymethyl cellulose, cellulose acetate, and chitosan.

Chapter 5 gives the preparation and characterization of PANI/MWCNTs/Starch composite materials.

Chapter 6 deals with the application for PANI/MWCNTs/Starch for hydrogen peroxide, glucose, and cholesterol sensing.

Chapter 7 contains the preparation characterization and application of PANI/MWCNTs/CMC composite material for ascorbic acid sensing.

Chapter 8 presents the comparative study of PANI-HCl, PANI-Citric acid, and PANI-lemon. We have successfully prepared PANI nanorods and used them for catechol sensing.

Chapter 9 deals with summary and conclusion of the thesis.

Chapter 1

Appendix:

Additional research data has been given appendix A, B, C, D.

Appendix A (chapter 5); Appendix B (chapter 6); Appendix C (chapter 7); Appendix D (chapter 8)