# Conducting polymers for flexible devices

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## ABSTRACT

Electronic wearable devices of the next generation, which are mechanically flexible and stretchable and need to fit the human body conformally, are in high demand. Organic and polymeric semiconducting materials have seen tremendous growth in energy harvesting systems due to their cheap cost, large-area manufacturing, high flexibility, low toxicity, and tunable electronic properties. The extraordinary characteristics of conductive polymers, such as lightweight, flexibility, and non-toxicity, make them intriguing options for next-generation stretchy, flexible, and wearable electronic systems.

## INTRODUCTION

Flexible electronic materials and technologies have received much attention due to their numerous applications in various fields, including healthcare monitoring, soft robotics, flexible displays, human-machine interfaces, and other areas.[1-3] For electrical devices to be flexible, the electrodes and active components have to be mechanically stretchable. Although metals can be relatively thin and still have significant mechanical flexibility, their Young modulus is substantially higher than elastomers, which are typically employed as the substrate for flexible electrical devices. Bulk metals are undesirable for use as transparent electrodes in optoelectronic devices like solar cells and light-emitting diodes (LEDs) due to their low transparency in the visible range of light. Flexible electronic devices can use solar cells and flexible LEDs for their displays and power sources. An optoelectronic device must have a transparent electrode on at least one electrode to produce or capture light. However, oxides like indium tin oxide (ITO) are most often used as transparent conductors. To serve as the flexible transparent electrode, they are too fragile. Inherently conductive polymers (CPs) and conductive nanomaterials are examples of potential flexible transparent conductors.[4-6] Using metal nanowires, especially silver (Ag) nanowires and carbon nanotubes (CNTs), substantial research has been done on the flexible transparent electrode for optoelectronic devices. In addition to their inherent conductivity, their resistance is also influenced by the contact resistance between the nanowires or nanotubes. However, the sheet resistance of CNT film is too low, which makes it difficult for practical use, whereas Ag nanowire electrodes have problems such as adhesion to the substrate, excessive roughness, and performance deterioration brought on by surface oxidation.[7, 8] Graphene is another intriguing possibility for the transparent electrode due to its severe transparency and high mechanical flexibility.[9] However, a thin graphene layer with remarkable homogeneity across a vast area is challenging to manufacture. Given its potential for high mechanical flexibility and intrinsic conductivity, conducting polymers are exciting candidates for the electrode.

The delocalization of electrons allows some conjugated polymers, referred to as conducting polymers, to conduct electricity. Outstanding electronic characteristics like large surface area, electrical conductivity, strong electron affinity, low energy optical transition, and mechanical flexibility result from this charge mobility. In 1977, Shirakawa et al. reported the electrical conductivity of these polymers for the first time found in polyacetylene.[10] Following that, these polymers drew much interest from academics and scientists because of their significant economic value, excellent environmental stability, tailored optoelectronic capabilities, practical mechanical qualities, and a host of other factors. They include polyaniline (PANI), polypyrrole (PPy), polythiophene (PTh), poly(naphthylamine) (PNA), polycarbazole (PCz), poly(o-phenylenediamine) (PoPDA), polyanisidine (PANIS) and poly(3,4-ethylenedioxythiophene):polystyrenesulfonate (PEDOT:PSS).[11-13] These have numerous uses, such as optoelectronic devices, electrochromic devices batteries, biomedical materials, sensing, environmental cleanup, and imaging devices [14]. Carbon-based compounds, which are electrically conductive polymers, have alternate single and double (or triple) bonds that enable charge transfer.

Essential elements of these materials' electronic state density include their macromolecular architecture, doping level, and crystallinity. A shift in state density from isolated states to a band-like structure is brought about by extending the degree of polymerization of π conjugated polymer chains, which causes a broadening of the π orbitals with significant overlapping. As a result, π conjugated polymers can be used to create electronic devices ranging from semiconductors, semimetals to metals. Heeger Alan J discovered the inorganic material $(SN)_x$ sulfur nitride metal, which becomes more electrically conductive when bromine is doped.[15] This discovery inspired the study of polyacetylene and led to the discovery of bromine doped polyacetylene with a conductivity that is a million times better than that of pure polyacetylene.[15] Tens of thousands to millions of monomer units are used for building traditional polymers. A conjugated polymer chain is nonetheless stiff and soluble in solvents despite having fewer monomer units than conventional polymer chains. It possesses mechanical characteristics because the single and double bonds alternate. The linked side chains of conducting polymers, which also give them their mechanical, electrical, and optical characteristics, are primarily responsible for their solubility and processability.[16] Conducting polymers are partially crystalline and amorphous. Conducting polymers can exist in both localized and delocalized forms, and the disorder has a significant impact on the delocalization of π - bonds. The production of charge carriers like polarons, bipolarons, solitons, and other particles responsible for the transition from insulator to metal depends on this delocalization. Conjugated polymers' conductivity behaves as an insulator to semiconductors in their pure form and increases with dopant concentration.[17] When doped or exposed to light, the π bond in conjugated polymers self-localizes to experience nonlinear excitation as polarons, solitons, bipolarons, etc. The polymer then transforms from a nonlinear excitation state to a metallic state.[18]

## TYPES OF CONDUCTING POLYMERS

### A. Polyacetylene

The fascinating properties of the traditional conjugated polymer Polyacetylene (PA), a linear polyene chain [-(HC=CH)-] as shown in figure (1), make it an excellent candidate for application in electrical devices. These include the production of supramolecular assemblies, chiral recognition, helical graphitic nanofibers, gas permeability and liquid crystallization.[19, 20] Other characteristics include high electrical conductivity and photoconductivity. PA is one of the most elementary organic polymers that can exhibit conductivity similar to metal.[10] Since the chemical structure of PAs contains repeating units of two hydrogen atoms, substituting other molecules for hydrogen atoms to produce mono- or di-substituted PAs makes it simple to add pendant groups to the chain.[19]

Non-doped PA electrical conductivity, which depends significantly on their conformation for cis- and trans-PA is $10^{-9}$ S/cm and $10^{-6}$ S/cm, respectively.[21] By comparison, PAs, through p- or n-doping, can reach an almost metallic conductive level ($10^{4}$-$10^{5}$ S/cm).[22, 23] Although PA has a promising potential to conduct electricity, its processing challenges and significant instability, even at ambient temperature have severely restricted its use in real-world applications.[24] The design and development of flexible devices have used PA less than other CPs with lower electrical conductivity but greater stability and processability. Precursor-assisted synthesis, catalytic and non-catalytic polymerization and other processes are used for synthesizing PA.[18] Catalytic polymerization methods like Ziegler-Natta or Luttinger catalysis are often used to polymerize acetylene and other monomers to synthesize PA and oligomers like cyclooctatetraene and vinyl acetylene.[25]. Zeigler-Natta catalysts, which are composed of Ti(0-n-$C_4H_9$) and $(C_2H_5)_3$ $A_1$, have a high solubility in organic solvents and excellent selectivity, making them ideal catalysts for producing highly crystalline PA films.[25]

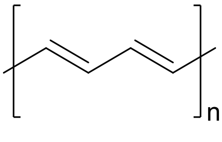


FIGURE 1: STRUCTURAL ILLUSTRATION OF POLYACETYLENE

### B. Polyaniline

Polyaniline (PANI) in Figure (2) is one of the most promising conjugated CPs owing to its superior environmental stability, high and adjustable electrical conductivity, high processability and optical properties.[26] PANI conductivity is significantly influenced by dopant concentration and pH; at pH < 3, it can have conductivity similar to that of metal.[27] Based on the idealized oxidation states of the aniline monomers, PANI exists in three different forms: leucoemeraldine $[(C_6H_4NH)_n]$, emeraldine $[([C_6H_4NH]_2[C_6H_4N])_2]_n$ and pernigraniline $[(C_6H_4N)_n$.[28] In the pernigraniline base (blue/violet), PANI is oxidized. In contrast, the emeraldine (salt-green/base-blue) is partially oxidized, and the leucoemeraldine base (white/clear) is completely reduced. At room temperature, PANI is more conductive and stable in its emeraldine form. Even with doping, the pernigraniline and leucoemeraldine forms show weak conductivity. PANI conductivity may be altered by immersing the emeraldine base in an aqueous acidic solution, which is highly depend on the manufacturing process.[29] The emeraldine base state is, however, weakly soluble and challenging to process due to the rigid polymer backbone and hydrogen bonding interactions between neighboring chains. Additionally, it has a limited range of practical applications due to its instability at melt-processing temperatures. In order to generate flexible electronics, functionalized PANI and other PANI derivatives are widely employed.[30] Functionalized PANI and other PANI derivatives are frequently used to create flexible electronics. PANI has received significant attention in the design and development of commercial technologies, exceptionally flexible electronic devices, in a variety of fields, including organic electronics[31], biosensors, photovoltaic cells, chemical sensors, corrosion devices, solar cells, electro-rheological material and organic light-emitting diodes.[32, 33] This is a result of its low cost, great optical and electrical qualities, excellent environmental stability, and strong mechanical and anti-corrosion capabilities.

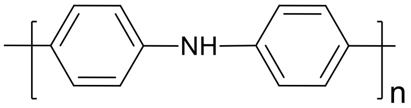


**FIGURE 2: STRUCTURAL ILLUSTRATION OF POLYANILINE**

**Poly [3,4-(ethylenedioxy)thiophene]**

Poly [3,4-(ethylenedioxy)thiophene] (PEDOT) in figure (3) is a common CP due to its ease of production, high conductivity, optical clarity and superior air stability.[34] In PEDOT crystals, inclined stacks with electrons that are lighter than holes are arranged in monoclinic lamellar structures.[35] The pseudo-orthorhombic unit cell in the PEDOT structural model has four monomers and one tosylate ion and the lattice parameters for the cell are 14.0, 6.8 and 7.8 Å correspondingly.[36] Due to its benefits, PEDOT has been widely used in constructing numerous flexible devices in bioelectronics, energy conversion, and sensors.[37] To boost its aqueous processability as a thin film, PEDOT must be coupled with hydrophilic surfactant additives like poly(styrenesulfonate) (PSS) due to its hydrophobic nature. PEDOT has good water dispersion because the long, water-soluble PSS molecular chains interact with the short, insoluble PEDOT chains via coulombic forces to form grains. PEDOT: PSS grains (30–50 nm in size) consist of tangles composed of multiple PEDOT segments and a single PSS chain. To reduce excess PSS and cause phase separation or morphological rearrangement and raise the electrical conductivity of PEDOT: PSS, a variety of processing techniques and doping agents have been employed.[38] Polar solvents, including ethylene glycol, dimethyl sulfoxide (DMSO) and co-solvents or acids like sulfonic acid, chloroplatinic acid and mineral acids, were used in these procedures to increase the conductivity of PEDOT:PSS films.

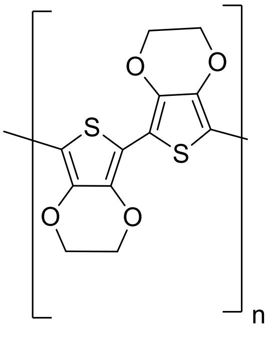


**FIGURE 3: STRUCTURAL ILLUSTRATION OF POLY [3,4-(ETHYLENEDIOXY)THIOPHENE]**

**C. Polypyrrole**

Polypyrrole (PPy) in figure (4) is a heterocyclic positively charged CP with N atoms when it is oxidized, enough oxidation can cause it to lose all conductivity.[39] Aqueous solutions and organic electrolytes both increase PPy's electroactivity. It is also highly fascinating since PPy is one of the most intriguing CPs due to its monomer (pyrrole), which is easily oxidized, widely accessible, lightweight, water-soluble, affordable and biocompatible.[40] High conductivity, strong redox characteristics and good environmental stability are also present. Because of this, PPy has been considered for a wide range of applications, including biochemical and electrochemical energy devices. PPy is also more adaptable than the majority of other CPs and may be coupled with other nanostructured materials, such as graphene or other carbon compounds to make nanocomposites. Due to their higher ion diffusion rates and bigger contact surface areas, these materials can have much better characteristics. Due to these outstanding characteristics, PPy is a serious competitor to meet the demand for flexible and portable electronic devices.[41]

Due to the alternating single and double bond structure of PPy, which results in a slight delocalization of the electron density within the molecule, it may be conducive.[42] A significant band gap energy of 3.16 eV exists in pristine PPy, an insulator.[43] Doping techniques using chemicals and electrochemistry have been used to increase PPy conductivity. In these doping techniques, PPy oxidation can remove an electron to change the neutral polymer chain's structure from benzenoid (aromatic) to quinoid. Doping can change PPy into an ionic complex with cations and added counter ions. The most popular PPy synthesis techniques employ chemical and electrochemical polymerization. Other cutting-edge polymerization methods, like electrospinning, micro-emulsion, ultrasonic irradiation, mechano-chemical polymerization, vapor-phase polymerization and photopolymerization, are now attracting people's attention to produce highly conductive PPy.[44]

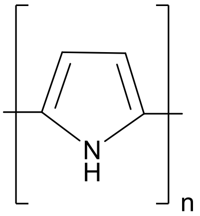


**FIGURE 4: STRUCTURAL ILLUSTRATION OF POLYPYRROLE**

### D. Polythiophene

Polythiophene (PT) in Figure (5) is a significant CP because of its straightforward structure, excellent stability and several optoelectronic characteristics. PT and its variations in both the undoped and doped states have attracted a lot of interest in sensing device applications due to structural modification and solution processability.[45] Additionally, it displays a strong affinity for adsorption on the electrode surface as well as a selective barrier effect against certain chemicals. In order to change the overall electronic properties, side-chain groups or dopants with a band gap between 3 and 1 eV can be used.[46] PT polymerization and deposition on large insulating surfaces have proven difficult because of the material's high oxidation potential. Thiophene monomers have been widely utilized to make polymeric thin films using various techniques, such as oxidative chemical vapor deposition, electrochemical oxidation and chemical oxidation in solution. Electrochemical oxidation is one among them. Because it is simple to manage the degree of polymerization, polymerization is the most widely used technology. Moreover, electrospinning can be used to form PT nanofiber architectures. One of the most significant classes of PTs is Poly(3-alkylthiophene)s (P3AT), which exhibit good electrical and thermal conductivity, processability and environmental stability.[45] However, P3AT is expensive. Thus, there are just a few feasible uses for it. Because they achieve a reasonable balance between the solubility and electric properties, poly(3-hexylthiophene), poly(3-pentylthiophene), and poly(3-butylthiophene) are well-known CPs that have been widely employed in organic electronic sensing applications. All of these substances belong to the P3AT family. It becomes possible to accomplish balanced hole/electron transport as the number of alkyl chains increases due to the continually increasing degree of phase separation.[45]

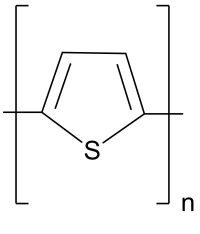


**FIGURE 5: STRUCTURAL ILLUSTRATION OF POLYTHIOPHENE**

## FACTORS AFFECTING CONDUCTIVITY OF CONDUCTING POLYMERS

Conducting polymers, as their name suggests, have the capacity to conduct electricity related to a particular mechanism. Thus the decisive variable, conductance, is a key characteristic that makes it crucial to use in a wide range of fields, including energy storage. Temperature, solvent, doping, polymerization technique, etc. are significant factors in controlling the conductivity of electroactive materials, including conducting polymers.[47]

### A. EFFECT OF POLYMERIZATION TECHNIQUE

For the synthesis of polymers from monomers, several polymerization procedures, including environmentally friendly ones, are used.

#### a. Chemical oxidation method

Lewis's acid, ammonium persulfate, and other oxidizing agents can oxidize the monomer and form cation and cation radical sites in it.[48] Two protons must be abstracted in order to form a covalent connection between monomer molecules, however, “head to head”, “tail to tail” and “head to tail” type linkages are rarely conceivable.[49] Chain growth and polycondensation are the two techniques used in chemical oxidative polymerization. In contrast to chain development, which involves electrophilic substitution, polycondensation involves the recombination of cation radicle oxidation sites.

#### b. Electrochemical polymerization

A simple, safe and ecofriendly method to convert monomer into conducting polymer is electrochemical polymerization, sometimes referred to as electropolymerization. This technique makes use of oxidant over a working electrode which initiates polymerization. This green polymerization method is free of harmful chemicals and has high reproducibility and good electrical and electronic characteristics.[50] Anodic electropolymerization and cathodic electropolymerization are the two common mechanisms that involve the oxidation of monomer over the substrate. The coupling of neighboring cations or interaction between neutral monomer or radical cation are two possible mechanisms of polymerization.

#### c. Vapor phase polymerization

This method makes use of vapor-phased monomer to a substrate to initiate the polymerization. The lack of solvent, the fact that monomer is a vapor component, which reduces the chance of agglomeration and moreover, the conductivity of the conducting polymer produced in this polymerization is high are the benefits of vapor phase polymerization than other methods.[51] The manufacturing of capacitors, organic solar cells and electrochemical energy storage devices are made possible by this method.

#### d. Photochemical method

Conducting polymers can also be made by exposing them to light and ultraviolet rays in the presence of a catalyst. According to the mechanism, there are two types of photochemical processes: the first is the excitation of monomers in the presence of light, and the second is photopolymerization in the presence of a suitable catalyst. The first approach is hardly ever used due to its low quantum efficiency and lengthy reaction time.[52]

### B. EFFECT OF DOPANT

Organic compounds can be doped with proton donors, long-chain components like camphor sulfonic acid (CSA), nitrosyl sulfuric acid (NSA), dodecyl benzene sulfonic acid (DBSA) and p-type (oxidative process) and n-type (reductive process) dopants to improve their electrical conductivity and solubility.[53] While p-type doping involves the oxidation of polymers by dopants and leaves them with a positive charge, n-type doping involves the reduction of polymers by dopants and leaves them with a negative charge on them. These dopants have the ability to enhance conductivity as well as electrical properties. Conducting character can be generated in conducting polymers using dopants that have two distinct kinds of charge carriers i.e. polarons and bipolarons in Figure (6). [54] The size, type and quantity of dopants used to dope polymers determine their conductivity. The size of the dopants used for doping purposes plays a significant role in the selection of the dopant process. The structural properties and conductivity of conducting polymers are effected by the size of the dopants which includes smaller dopants like Br, Cl, etc. as well as larger dopants like p-Toluene sulfonic acid (PTSA), dodecyl benzene sulfonic acid (DBSA). [55] Doping improves up to a certain point (maximum conductivity at a charge carrier density of $10^{18}$–$10^{21}$), but after that point, a negative trend emerges that can be associated with a change in the polymer's microstructure.[56] Since doping is reversible, dedoping can result in polymers having semiconductive characteristics.[47] Numerous doping methods are employed, including solution doping, self-doping, electrochemical doping, gaseous doping, radiation-induced doping (by irradiating with neutrons) and others.[57]

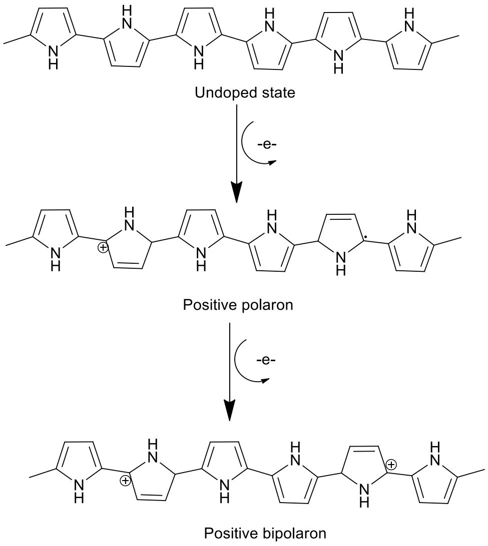


FIGURE 6: CHEMICAL STRUCTURES OF POLYPYRROLE POLARON AND BIPOLARON

### C. EFFECT OF TEMPERATURE

Temperature has a significant impact on the electrical conductivity of conducting polymers; as temperature rises, the material's resistivity significantly decreases as a result of the massive emission of free electrons (charge carriers), which causes high thermal excitation and increased electronic conduction.[47] Study shows that when temperature rises, limited conductivity changes occurs in samples that are heavily doped, but significant alteration occur in samples that have just moderately or lightly doped.[58] For a deeper understanding of electrical conductivity of conducting polymers, Arrhenius plots and Mott plots are often examined. In order to depict the interaction of charge carriers near room temperature, the Arrhenius equation (Equation 1) is used. The Mott plot also involves an analysis of the overlapping wave functions of nearby localized charge centers, which can be obtained using the Mott equation (Equation 2).[59] The temperature is shown to have a significant impact on or be a function of conductivity of conducting polymer.

Arrhenius equation:

$$\sigma = \sigma_O \exp\left(-\frac{E_a}{kT}\right) \qquad (1)$$

where $\sigma$ is conductivity, $E_a$ is activation energy, $\sigma_O$ is DC conductivity, k is Boltzmann constant and T is absolute temperature.

Mott equation:

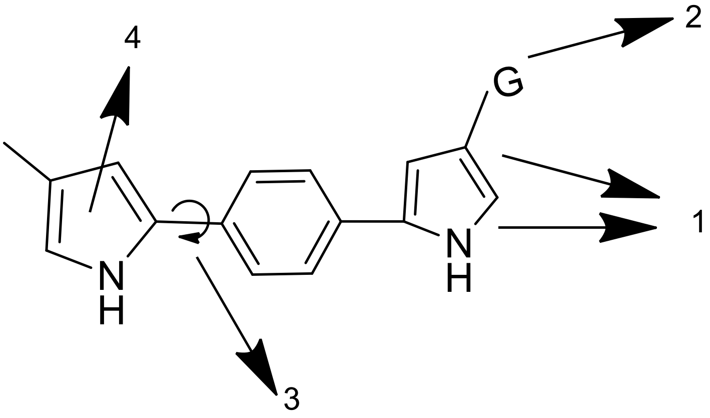
$$\sigma = K_0 T^{-1/2} \exp\left[-\left(\frac{T_O}{T}\right)^{1/4}\right] \qquad (2)$$

where σ is conductivity, $K_o$ is Mott characteristic conductivity parameter, T is absolute temperature, $T_o$ is Mott characteristic temperature.

According to Yamada *et al.*, the temperature drops results in decrease in charge carrier density.[60] Camphor sulfonate doped PPy film prepared electrochemically at varying temperatures for supercapacitor indicates that conductivity drops as the temperature increases (10-30˚C being optimum temperature).

### D. EFFECT OF BANDGAP

The bandgap, which refers to the energy (Eg) needed to excite an electron from the conduction band (CB) to the valence band (VB) in inorganic semiconductors or from the highest to the lowest occupied molecular orbital (HOMO to LUMO) in organic semiconductors, is a distinctive property of conducting materials (metals or semiconductors). [43] [61-64] The conductivity of conducting polymer is strongly influenced by the band gap; the larger the band gap, the lower is the conductivity. In conducting polymers, variations in the bond length may be utilized as a predictor of the bandgap; a bigger bandgap is caused by a greater variation in the C-C bond length, which results in less conductivity. In addition to the bond length change, additional elements in Figure (7), include planarity, the resonance energy of the conjugated structure, п- conjugation length, the presence of substituents and their effects, the dihedral angle (θ), intermolecular interactions, etc. [65] Conducting polymers are typically large bandgap insulators that have further processing to become conductors by oxidation or reduction. According to Reyes et al., the difference between HOMO and LUMO decreases as the size of the non-substituted oligomer furan increases, increasing conductivity. In addition, substituted oligomers have lower bandgap energy than a non-substituted oligomer and the polyfuran can exist in dicationic (0.15eV) and dianioninc (0.17eV) forms.



1. Bond length alteration ; 2.Substituent ; 3.Planarity ; 4. Resonance

**FIGURE 7: STRUCTURAL FACTORS AFFECTING BANDGAP IN CPs**

### E. EFFECT OF EXTENDED CONJUGATION

The extent of conjugation directly correlates with the electrical conductivity of conducting polymers (a low degree of π conjugation leads to low electrical conductivity). [66] Semiconducting devices make use of conducting polymers due to their optical and electrical properties, especially the small band gap and extended conjugation. An organic polymer with a conjugated system named PA can develop a high electrical conductivity (17000 S/cm) when doped with iodine. According to the studies, the electrical conductivity of trans-PA drops by eight times when the conjugation length is reduced from 100 Å to 10Å.

### F. EFFECT OF FUNCTIONAL GROUPS

The redox potential, stability and conductance of conducting polymers are all influenced by the type of functional groups, such as electron withdrawing groups (EWG) or electron donating groups (EDG), which are present in the molecule. The steric and electronic effects of functional groups on conducting polymers induce change in their electrical, electrochemical and several other physical characteristics, depending on position, number and type of substituents. The type of functional groups and steric or electronic effects have a significant impact on the redox properties of PANI. The EWG decreases the oxidation potential, whereas the EDG increases it by reducing the electron density on the nitrogen atom. With increased distance between the polymer units, EDG such as –CH3 was discovered to decrease the steric strain by increasing the torsion angle between the conjugated rings.[67]

## APPLICATIONS OF CONDUCTING POLYMERS

The electrical characteristics, high theoretical capacitance, strong redox activity, good wave absorption and superior electrochemical behavior of conducting polymers make them useful in a wide range of applications. A few are explained here:

### A. SUPERCAPACITORS

Supercapacitors have attracted tremendous commercial attention because of growing markets for electronic automobiles, wearable gadgets, etc. The key difference between supercapacitor technology and conventional capacitors is that the former can store 1000 times more energy. In addition, they include high energy and power densities, high speed charge discharge cycle and outstanding cycle life.[68] There are three types of supercapacitors based on how they store their charge. An electric double layer capacitor (EDLC) uses non-faradic method to function and the interaction between the electrode and electrolyte is where the charge builds up. A double layer of charge develops during an electrochemical reaction that causes capacitance. The faradic mechanism used by pseudocapacitors stores charge by a redox reaction or intercalation. The redox activity of conducting polymers [69] and transition metal oxide such as $Co_3O_4$ [70], $Mn_3O_4$ [71] make them used as electrodes for pseudocapacitors. EDLCs and pseudocapacitors combination have been used in hybrid supercapacitors.

Conducting polymers are the most promising active electrode when compared to the common active electrode materials because of their intrinsically flexible polymeric nature, making them ideal for supercapacitor application.[72] A variety of morphologies, including particles, rod-like structures, sheets and hydrogels, are obtainable for conducting polymers. [73]

Kulia *et al.* developed a sequential array of vertically aligned PANI nanorods utilizing a nanotemplate based on supramolecular assemblies of block copolymer on transparent indium tin oxide (ITO) substrate. The greatest capacitance of the nano-spaced PANI nanorod arrays, which had outstanding electrochemical characteristics, was 3407F/g.[74] Up to 500 cycles the PANI nanorods exhibit high electrochemical stability, but beyond that, they act irregularly and do not exhibit a regular charge-discharge cycle. This may be due to the less stability of small dimension PANI nanorods. Wang Kai prepared a large array of aligned PANI nanowires by the galvanostatic current method. [75]When PANI was employed as the supercapacitor electrode, the huge arrays of nanowires had very narrow diameter and were positioned perpendicular to the substrate, which aided in ion diffusion as illustrated in Figure (8). PANI nanowire arrays' maximum specific capacitance, which was measured at 950 F/g, was recorded. The orientation of nanostructures could dramatically enhance the electrochemical performance of functional nanomaterials. [75]

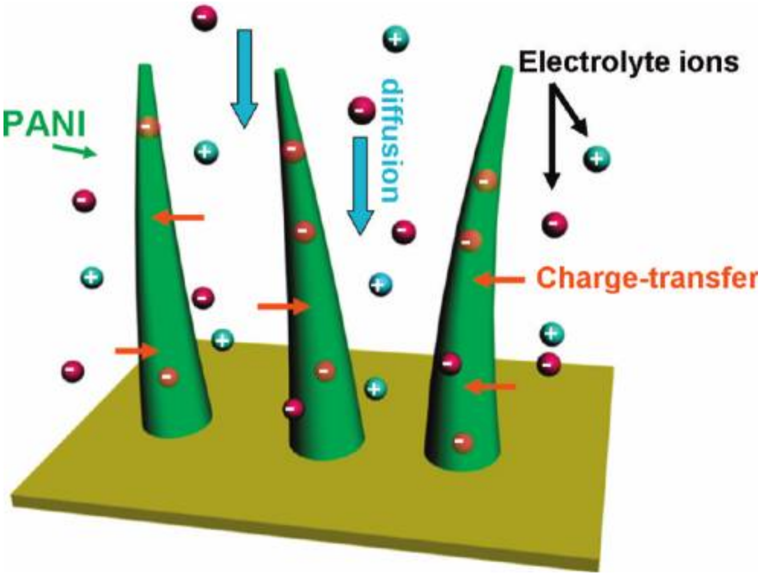


**FIGURE 8: SCHEMATIC ILLUSTRATION OF THE OPTIMISED ION DIFFUSION PATH IN NANOWIRE ARRAYS.** Reprinted with the permission from [75,] copyright 2010, American Chemistry Society.

Afsaneh *et al.* designed and fabricated a high-performance asymmetric supercapacitor with a novel ternary binder-free nanocomposite (PPy/FeCoS-rGO/NF) consisting of polypyrrole, iron-cobalt sulfide and reduced graphene oxide on nickel foam electrode as shown in Figure (9). 3D porous graphene foam (GF) not only enhances the uniform development of conductive PPy film and FeCoS ultrathin porous nanosheet but also considerably increases the mechanical stability, rate capability and energy storage capacity. With a high specific capacitance of 3178F/g at 2A/g and an acceptable rate capability, the PPy/FeCoSrGO/NF demonstrates exceptional electrochemical characteristics. Superior electronic conductivity, high surface area, low contact resistance between the PPy/FeCoS-rGO active layer and the Ni foam current collector, a short diffusion pathway for electrolyte ions, quick electron transfers and efficient use of active material during Faradic charge-storage processes are all factors that contribute to the excellent electrochemical performance. A hybrid asymmetric supercapacitor is produced by using nickel foam coated with reduced graphene oxide (rGO/NF) as the negative electrode and PPy/FeCoS-rGO/NF as the positive electrode by taking advantage of their superior characteristics. A device made of PPy/FeCoSrGO/rGO has a high specific capacitance of 94 F/g at 1 A/g. With 97.5% capacitance retention after 2500 cycles, the asymmetric supercapacitor device exhibits exceptional cycling performance.[76]

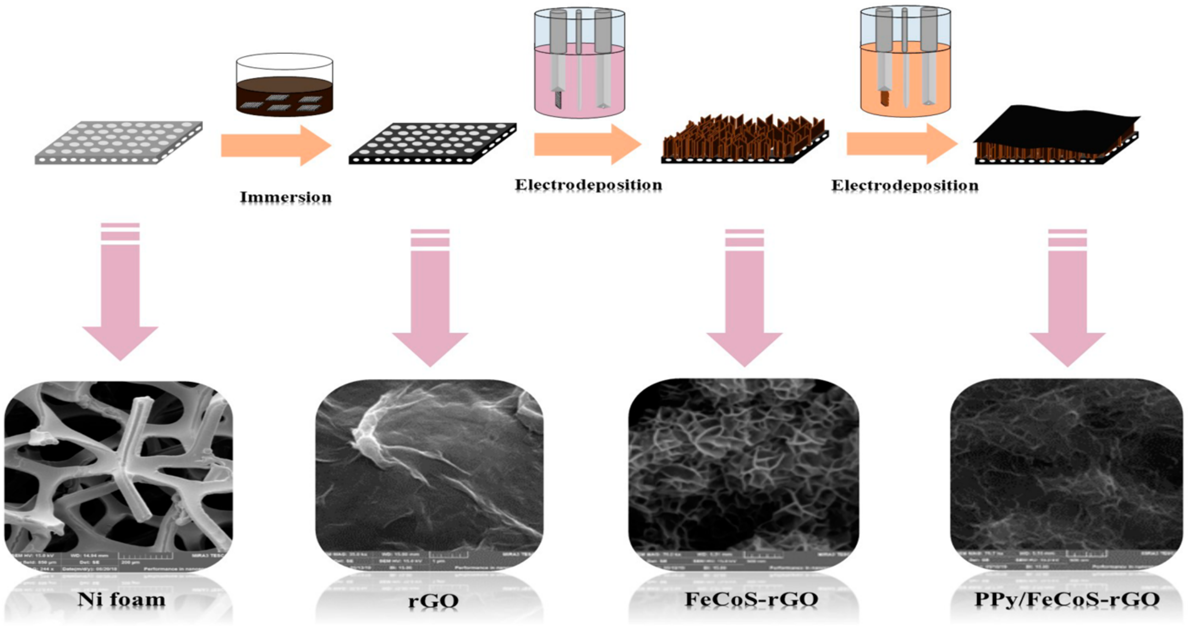


**FIGURE 9: SCHEMATIC ILLUSTRATION OF PREPARATION OF PPy/FeCoS- rGO ELECTRODE ON Ni FOAM SUBSTRATE.** Reprinted with the permission from [76,] copyright 2020, American Chemistry Society.

Anthony *et al.* demonstrated a quick and easy approach for depositing a very reliable pseudocapacitive substance based on a simple drop-cast of a commercial PEDOT: PSS solution on 3 nm alumina coated silicon nanowires in Figure (10). It was feasible to combine epitaxially grown and highly doped silicon nanowires with a protective alumina atomic layer deposition (ALD) coated layer and embed them in a gelatinous-like polymer matrix. A specific capacitance of 3.4 mF/cm$^2$ at a current density of 2 A/g in an aqueous $Na_2SO_4$ electrolyte was displayed by the composite material created PEDOT: PSS –Alumina coated Si Nanowires (PPSS-A@ SiNWs), exhibiting outstanding capacitive behavior. Micro supercapacitor (MSC) devices based on this material demonstrate exceptional lifetime capacity, maintaining 95% of its original capacitance after more than 500 000 cycles at a current density of 0.5 A/g. [77]

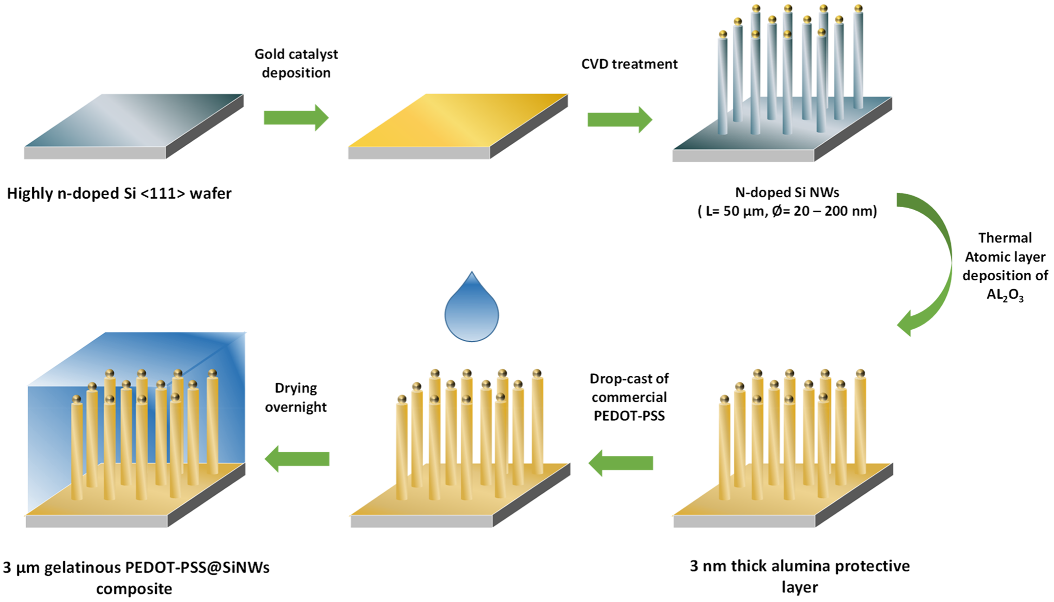


**FIGURE 10: SCHEMATIC ILLUSTRATION OF MICRO SUPERCAPACITOR ELECTRODE MANUFACTURING INCLUDING CHEMICAL VAPOUR DEPOSITION, ATOMIC LAYER DEPOSITION AND DROP CAST.** Reprinted with the permission from [77] copyright 2018, American Chemistry Society.

## B. CORROSION INHIBITION

Metals are anticipated to be employed in the construction, automobiles, energy, aerospace, home sectors, etc. Metals rapidly deteriorate when exposed to moisture, acid or alkaline or both environments. Corrosion inhibition techniques and coatings have been attributed to preventing the attack on them. Earlier cathodic and anodic inhibitors make use of chromate coatings. The main disadvantage of chromates and coatings containing chromium is that they are carcinogenic and hazardous to both human life and the environment. Conducting polymers and conducting polymer pigmented coatings considerably enhances corrosion prevention. Conducting polymers has drawn increasing interest as a possible component of corrosion-resistant coating systems because of their capacity to maintain the continual passivity of metal through anodizing and $O_2$ reduction on the film's surface. Between metal and coating, a metal oxide interface layer is formed. Listed below are the processes behind polymers' corrosion inhibition property:

- **a.** An electric field is produced when conducting polymer and metal comes in contact. The movement of electrons from metal to oxidized species is constrained by this electric field. As a result, corrosion is inhibited.[78]
- **b.** Anodic protection mechanism: in this mechanism, the metal oxide layer can be produced by polyaniline both above and below the metal surface. The metal oxide layer serves as a major source for corrosion inhibition.[79]
- **c.** Conducting polymers, particularly polyaniline, have the controlled release of inhibitors upon reduction. When the reduction takes place, an anion will be released from a conducting polymer based coating that has been applied to the metal surface. This helps in the reduction of corrosion.[80]

Sathyanarayanan *et al.* demonstrated vinyl acrylic organic and polyaniline pigmented epoxy. Its performance has been evaluated on stainless steel. Impedance spectroscopy first decreases due to the pinholes generated on the metal surface, then increases as exposure duration rises. As the exposure time extended, a metal oxide interface layer between the metal surface and below the coating was absorbed by the coating.[81] Hence it was concluded that the effectiveness of polyaniline pigmented organic coatings for corrosion inhibition coating depends on the exposure time and coating thickness.

Armelin *et al.* examined polyaniline and polypyrrole as anticorrosive additives in zinc epoxy coating, and their performance was examined separately. By exhibiting reversible redox properties akin to chromate coatings, it demonstrates that the corrosion prevention property was enhanced. Zinc pigments form zinc oxide, which protects the metal layer and reduces the possibility of corrosion. Additionally, the study showed that polypyrrole percentage above a particular threshold cannot demonstrate superior inhibitory properties.[82] Chen Fei and Liu Peng illustrated a new method of development of Polyaniline (PANI)-containing coatings for aqueous corrosion prevention demonstrated in Figure (11).[83] First, conducting polyaniline/partially phosphorylated poly (vinyl alcohol) (PANI/P-PVA) spherical nanoparticles with notable water dispersibility were produced by chemical oxidative dispersion polymerization in the presence of partly phosphorylated poly (vinyl alcohol) (P-PVA). A dipping technique was used to create and apply the aqueous PANI/P-PVA-containing coatings on mild steel. A salt spray test and electrochemical impedance spectroscopy (EIS) approach in 3.0 wt% sodium chloride aqueous solution were used to examine the corrosion protection capability of PANI/P-PVA-containing coatings on mild steel. The waterborne PANI/P-PVA-containing coatings with the PANI/P-PVA of 2.5 wt% were able to provide higher corrosion protection than the PANI nanoparticles in the emeraldine salt form (PANI ES) containing coatings with the PANI ES content of 2.5 wt% due to the effective $Fe_2O_3$ passive layer and uniform distribution of the system, as shown by the variations in the open circuit potential (OCP) values and EIS spectra with time of exposure.[83]

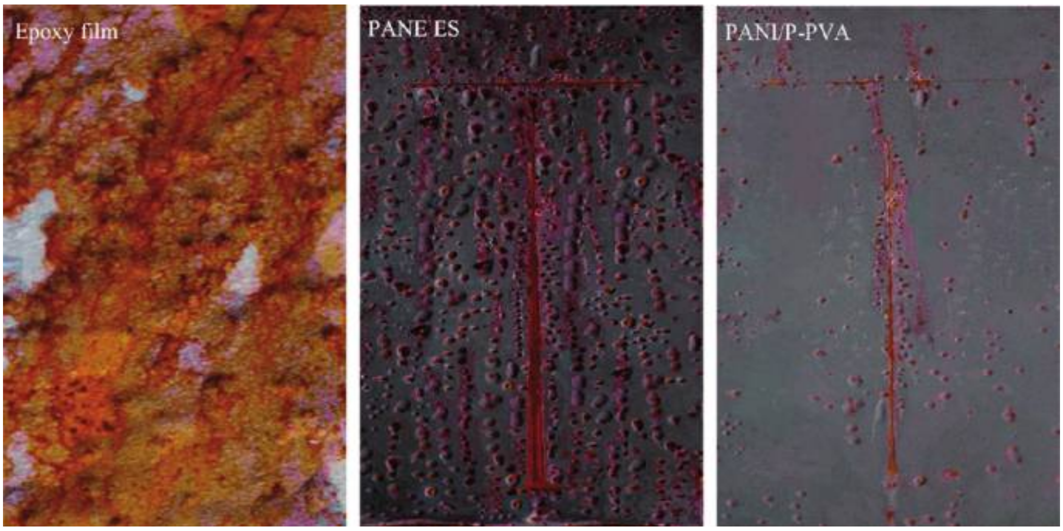


**FIGURE 11: PHOTOGRAPHY OF PURE EPOXY COATED PANEL, 2.5 WT % PANI ES-COATED PANEL AND 2.5 WT % PANI/P-PVA-COATED PANEL AFTER 30 DAYS EXPOSURE TO SALT SPRAY TEST.** Reprinted with the permission from [83]copyright 2011, American Chemistry Society.

The PANI/$TiO_2$ coating demonstrated high thermostability, anticorrosive and hydrophobic characteristics. Heat dissipation increases by thermal conductivity; hence thermal conductivity plays an important role in durability. It prevents thermal expansion-related coating delamination. The contact angle of PANI/$TiO_2$ was 150˚, which clearly indicates the super-hydrophobicity of the material.[84]

### C. GAS SENSORS

Gases produced by industrial and natural processes need to be recognized and analyzed due to their considerable impact on human health. Due to its advantages, such as adjustable conductivity (from insulator to metallic conductivity), low density, room temperature operation, affordability, environmental stability and many functionalization options, gas sensors made from conducting polymer sensing materials have generated interest. Gaseous ammonia ($NH_3$) is a prominent air contaminant. Although it is safe in modest doses, large amounts may lead to the destruction of the mucosa in the respiratory tract, eye and skin irritation and even death. Animal husbandry, production of urea for agricultural use, automobile exhaust and industrial manufacture are all sources of ammonia in the air. Polypyrrole and polyaniline are the conducting polymers that are most frequently used for gas sensors whose mechanism is shown in Figure (12).[85]

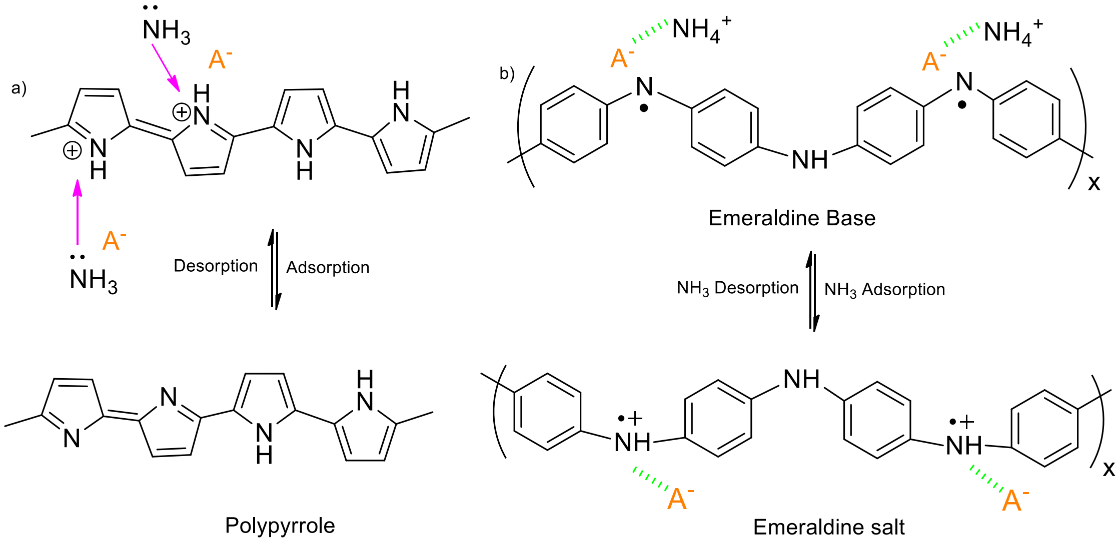


**FIGURE 12: AMMONIA SENSING MECHANISM BY a) PPy b) PANI BASED GAS SENSOR**

She Changkun *et al.* manufactured polypyrrole based gas sensor involving the comparison of two flexible substrates, sponge and silk-fiber.[86] The in-situ chemical oxidation approach was used to produce the PPy film using silica nanospheres (NS) as a template. When exposed to 100 ppm $NH_3$ in (68 ± 5%) relative humidity at room temperature, the response from the PPy/NS@ silk fiber sensor (73.25%) was five times larger than that from the PPy/NS@ sponge sensor (14.51%). Furthermore, the silk fibers serve as a reliable base for the attachment PPy, and the PPy/Ns@ silk fiber sensor has more active sites to provide a high sensing response and strong dynamic response.[86] Lalit *et al.* fabricated flexible PANI -polyethylene terephthalate (PET) ammonia sensors through in-situ polymerization processes at various temperatures. At room temperature, this flexible PANI sensor displayed high stability, good responsiveness, reproducibility and low detection limit (5ppm) to ammonia vapors. The sensor's resistance almost remains the same after repeated bending and its sensing capability is unaffected, indicating the sensor's mechanical stability and flexibility.[87]

The dual role of PANI in boosting flexibility and ammonia sensing performance was examined by Maity Debasis *et al.* [88]. Spray-coated MWCNTs on polypropylene woven fabric were used to produce the wearable, which was then chemically polymerized via in-situ polymerization in Figure (13). The sensor changed its resistance in response to ammonia vapors extremely fast (almost 9 seconds), and it swiftly returned to its baseline resistance when ammonia was not present (recovery time: 30 seconds). MWCNTs/PANI sensors have been shown to be particularly sensitive to ammonia in the presence of possible cross-interfering gases. After a month of monitoring, the sensor has displayed outstanding sensing stability. [88]

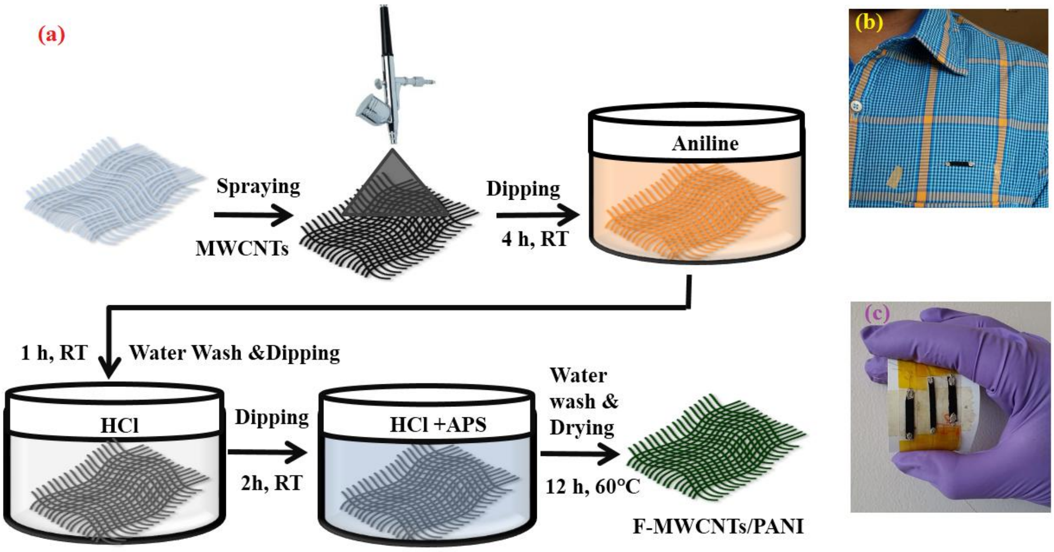


**FIGURE 13: a) SCHEMATIC SHOWING SPRAY DEPOSITION OF MWCNTs ON THE (F-MWCNTs) AND PANI SYNTHESIS ON MWCNTs COATED FABRIC SURFACE, b) SENSOR INTEGRATION IN SHIRT AND c) SENSOR ARRAY FOR AMMONIA SENSING.** Reprinted with the permission from [88] copyright 2018, American Chemistry Society.

He Yuan *et al.* described the development of an oxidant-intermediated surface polymerization (OISP) technique to manufacture conductive polymer coatings and patterns on a range of substrates. Spin coating, dip coating, or printing were used to deposit a coating or pattern made up of tightly packed colloidal vanadium oxide ($V_2O_5$-$nH_2O$) nanowires on Polyethylene terephthalate (PET) substrate. This coating or pattern is then transformed into a conducting polymer via in situ oxidation polymerization. The coating technique offers a simple means of integrating a varied CP pattern on a small substrate, making it appropriate for manufacturing sensor arrays. The same PET substrate was used to print three $V_2O_5$-$nH_2O$ patterns, which were afterward transformed into CP such as PPY, PANI and PEDOT as in figure (14A). After carbon electrodes were printed, each CP pattern was constructed into a resistor type sensor. Since each analyte and each CP had unique interactions, each sensor's signal amplitude S differed greatly. Each sensor's resistance was altered when analyte gas was added, and three channels of relative resistance change signals ($S = \Delta R/R$) were collected as a result. The signal amplitude S of each sensor was considerably distinct because the interactions between each CP and each analyte were distinct. The points (P1 and P2) corresponding to the various analytes will be placed in the various regions of the coordinate system if the three signals SPPY, SPEDOT and SPANI are combined to create two new variables, P1 = SPPY/SPEDOT, and P2 = SPPY/ SPANI. Figure (14B) demonstrates how sensor array allowed to discriminate between the vapors of ammonia, methanol and n-hexane based on their positions in the P1-P2 plot. The region was relatively independent of the analyte concentration. Therefore, using the position of the points (P1 and P2) in the plot, the aforementioned cross-reactive sensor array helps to detect an unknown sample that might be one of the three vapors mentioned above. [89][89]

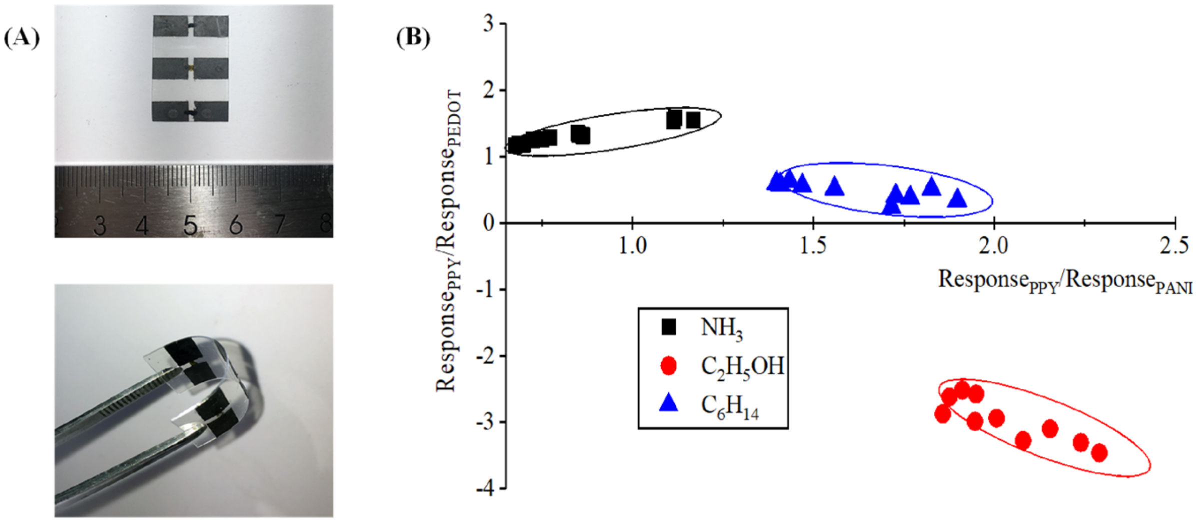


**FIGURE 14: GAS SENSING PERFORMANCE OF A FLEXIBLE SENSOR ARRAY FABRICATED WITH OISP (A) PHOTOGRAPHS OF FLEXIBLE SENSOR ARRAY MADE FROM PPy, PANI AND PEDOT FILMS. (B) PERFORMANCE OF THE SENSOR ARRAY IN DISTINGUISHING DIFFERENT GASES.** Reprinted with the permission from [89]copyright 2021, American Chemistry Society.

### D. CONDUCTING POLYMER HYDROGELS (CPH) FOR BIOELECTRONICS

Hydrogels and conducting polymer are combined to produce conducting polymer hydrogels, which have unique features that are not possible with traditional materials. The CPH are composed of hydrophilic networks that are covalently or physically cross-linked with conducting polymers like polyaniline, polypyrrole, or polythiophene.[90] High self-healing, electrical, mechanical and biocompatibility are characteristics of CPH. Tissue engineering and bioelectronics make extensive use of it. Conducting polymer is inadequate for certain applications and is substituted by CPH due to its long-term stability. Various techniques, such as Michael-type addition polymerization, click chemistry and free radicals, are utilized for the manufacturing of CPH. Human's reasoning ability, muscular motion and thinking are all made possible by the electronic response of the nervous system. Electrodes that interact with biological tissues make up bioelectronics interfaces. They gather bioelectronic signals and provide customized tissue self-monitoring.[91] The use of bioelectronics has been widespread in many fields, including electronic skin, wearable, flexible implanted devices and the monitoring of brain activity.[92]

Ren Xiaoning *et al.* illustrated highly conductive PPy-PEDOT: PSS hybrid hydrogels made using a simple solution-mixing process. [93]. A pyrrole monomer and a PEDOT: PSS dispersion were combined in this manufacturing method, and then polypyrrole (PPy) was synthesized in-situ using chemical oxidative polymerization. Hybrid PPy-PEDOT: PSS hydrogels were produced by the electrostatic interaction between negatively charged PSS and positively charged conjugated PPy. The PPy-PEDOT: PSS hybrid hydrogels have a conductivity of 867 S/m. The hybrid hydrogels of PPy - PEDOT: PSS exhibits high biocompatibility. The hierarchical porosity nature of the PPy-PEDOT: PSS hybrid hydrogels makes it easier to support 3D cell growth inside the hydrogels in Figure (15). The outstanding in situ biomolecular detection and real-time cell proliferation monitoring capabilities of the PPy-PEDOT: PSS hybrid hydrogels implies their potential as extremely sensitive electrochemical biosensors for bioelectronics applications.[93]

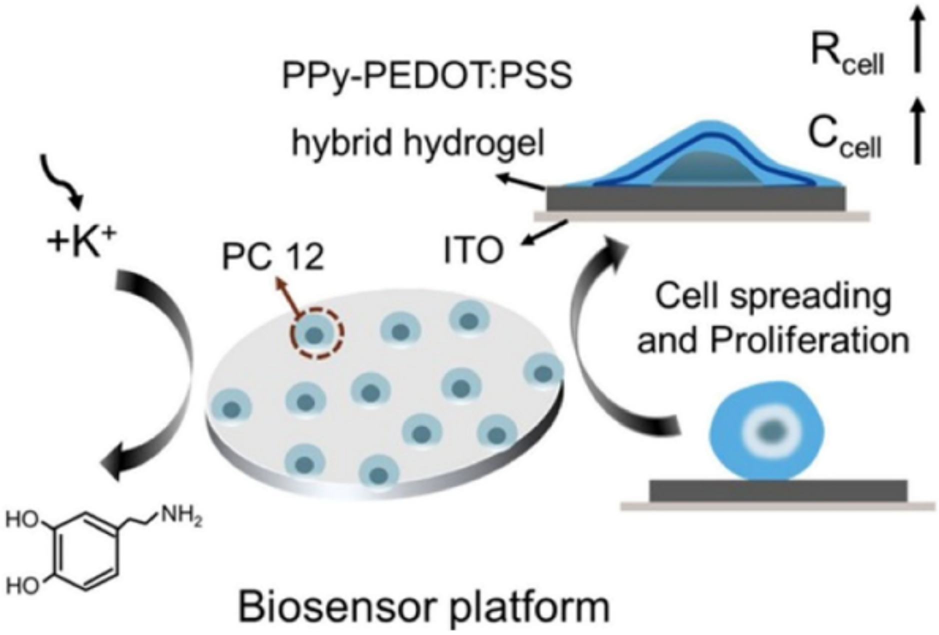


**FIGURE 15: REAL-TIME MONITORING AND IN-SITU SENSING OF LIVING PC12 CELLS USING PPY-PEDOT: PSSHYBRID HYDROGEL BASED BIOSENSORS.** Reprinted with the permission from [93] copyright 2021, American Chemistry Society.

In order to develop pressure and strain sensors, CPH are utilized because they can convert mechanical impulses to electrical signals. CPH based flexible electrodes are frequently employed to monitor electrophysiological signals, including electromyography, electroencephalography and ECG. Electrophysiological signals are often quite weak. The main fabrication challenges for the device are improving conductivity and signal-to-noise ratio. Biocompatibility, long-term stability and skin adhesion are further considerations. To recognize diverse electrophysiological signals, hydrogels consisting of PAA/PEDOT have been produced. Polyaniline-based hydrogels are used to monitor glucose and lactate in real-time.[94]

Conductive fillers can be added to boost their conductivity. Chen Po-Yen et al. developed a facile phytic acid mediated synthesis technique for PANI CPH, which shows a conductivity of 0.21S/cm.[95] . The formation of uniformly dispersed MWNT-phytic acid complexes was made possible by the inclusion of multi-walled carbon nanotubes (MWNTs). The production of MWNT-PANI composite hydrogels was favored by the polymerization of PANI on the surface of MWNT. This results in increasing conductivity to 1.54S/cm. [95] The hydrogels exhibit phase separation between the polymer matrix and filler if the filler loading exceeds a certain level which results in reduced mechanical stretchability. This drawback can be rectified by the incorporation of plasticizer into the polymer matrix. The stretchability of the conducting polymer PEDOT: PSS was improved by 35% after solvent annealing, which altered the fibrillary structure's interconnectivity.[96]

### E. BIOMEDICAL AND ANTIMICROBIAL APPLICATION

Near-infrared (NIR) photothermal treatment (PTT) is a potential technique for eliminating cancer cells within the human body. Fiber optics are used to light the target region. The use of photothermal materials to kill cancer cells appears to be less invasive when compared to other kinds of treatment like chemotherapy or radiation. PTT's targeted action, above other therapies, is one of its key benefits. This method reduces tissue loss around the active sites. As photothermal materials for PTT, materials with a high level of photostability, good NIR absorption, nanoscale dimension, low toxicity and less photocorrosion have a lot of possibilities. Conducting polymers such as polypyrrole, PEDOT and PANI have exceptional IR absorption capabilities and significantly lower cytotoxicity in Figure (16). Mei Chen *et al.* used polypyrrole as a photothermal material to investigate the 4TI tumor model's control growth [97]. According to an experimental investigation employing in vivo and in vitro evaluations, polypyrrole has a photothermal efficiency of 44.7% and exceptional cancer cell ablation capability under NIR irradiation of $1W/cm^2$. All irradiation tumors vanished after 60 days of treatment and no tumor development was recorded when the tumor size was evaluated at regular intervals.

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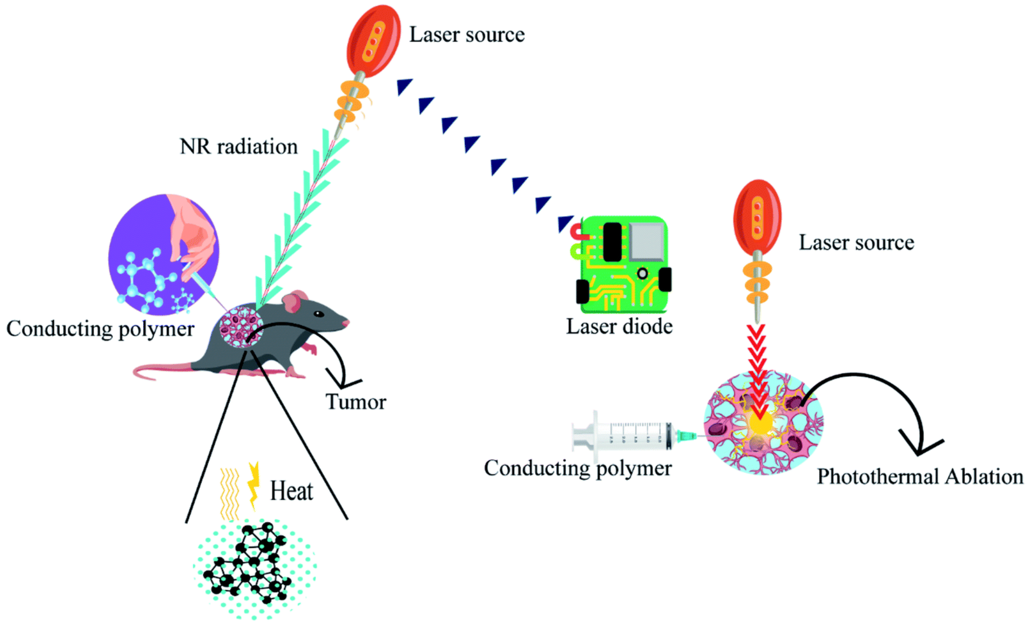

**FIGURE 16: PHOTOTHERMAL TREATMENT SCHEMATIC REPRESENTATION USING CONDUCTING POLYMER.** Reprinted with the permission from [18] copyright 2021, Royal Society of Chemistry.

With their strong NIR absorption, good water dispersion, perfect size and high photothermal efficiency of 48.5%, synthesized polyaniline composites have a promising future in photothermal therapy. Zero toxicity is a vital quality that supports in vivo research. The carbonaceous materials, such as graphene, graphene oxide, and reduced graphene oxide, are suitable PTT materials due to their high surface area, NIR absorption and effective heat conversion. However, their use has been constrained by their poor dispersity.[98] High photothermal activity of polypyrrole is directed toward cancer cells. Without changing the surface of the material, Chen and his coworkers examined the photothermal effectiveness of polypyrrole against 4T1 cancer cells. Both in vivo and in vitro analysis are possible by the biocompatibility of polypyrrole. Investigation revealed that polypyrrole has a 44.7% photothermal conversion efficiency and a high ablation efficiency due to its strong NIR absorption. The antibacterial effect of conducting polymer materials suggests that they could perhaps be used in biomedical and other smart materials. They have the ability to increase the amount of $H_2O_2$, which encourages the generation of hydroxyl radicals and their subsequent antimicrobial actions. Studies have been done on PANI coated cloth that has been doped with phytic acid, which results in improved crosslinking between the PANI and the substrate. Electrostatic interaction between the polymer backbone and the bacteria is what causes antimicrobial activity. The antibacterial activity of PANI-coated cotton and the polyester fabric was tested in Mueller-Hinton agar (MHA) against Gram-positive Klebsiella pneumoniae (K. pneumonia), Gram-negative Escherichia coli and Gram-positive Staphylococcus aureus (S. aureus) incubated for 18 hours at 37 °C. The investigation reveals that polyaniline coated polyester fabric has a better inhibition zone of 10.3 ± 0.04714, whereas cotton fabric exhibits no inhibition zone in the case of Escherichia coli (E. coli) or Klebsiella pneumonia (K. pneumonia).[99]

Several sectors such as the medical field, the food sector, the coating industry, etc., make use of conducting polymers as antimicrobial and antifungal agents. Polyaniline and other conducting polymers have antibacterial effects against Campylobacter jejuni, Staphylococcus aureus, Pseudomonas aeruginosa and Escherichia coli. The effectiveness of the composite material made of gold @ PANI-itaconic acid- iron oxide [Au@PANI-IA-Fe3O4] against Escherichia coli (Gram negative) and Staphylococcus aureus (Gram positive) germs has been tested in Mueller-Hinton agar (MHA) plates. It has been discovered that the composite presents a minimal inhibition zone for E. coli bacteria but a more effective zone of inhibition for Staphylococcus aureus with increasing composite concentration. Candida albicans has been used as a test subject for antifungal property of composite. The outcome demonstrates that the composite exhibits a tendency towards increase in inhibitory zone when the composite concentration increases. [100]

### F. AS AN ELECTRODE FOR ENERGY HARVESTING

Flexibility is one of the essential properties of the material under examination that aids the electrode materials in resisting external forces and the possibility of deformation. PANI, PPY, PTH and PEDOT are examples of CPs that can serve as electrodes in energy storage devices because of their high conductivity, low cost, and great mechanical flexibility etc. Park Byung-Wook et al examined the usage of CP in dye sensing solar cells in Figure

(17). [101] As a counter electrode (CE) in a dye-sensitized solar cell (DSC), conducting polymer poly(3,4-ethylenedioxythiophene) (PEDOT) doped with iron(III) tris-p-toluenesulfonate (PEDOT:Tos) with metallic conductivity was spin coated onto fluorine-doped tin oxide (FTO) glass and plain glass substrates for devices with cobalt-based redox electrolyte. Impedance spectroscopy indicated that the PEDOT:Tos-based counter electrodes in DSCs had a charge-transfer resistance that was five to ten times lower than the Pt/FTO CE. DSCs with PEDOT:Tos/glass CE yielded power conversion efficiencies (PCE) of 6.3%, similar to that of DSCs with platinized FTO glass CE (6.1%). [101]

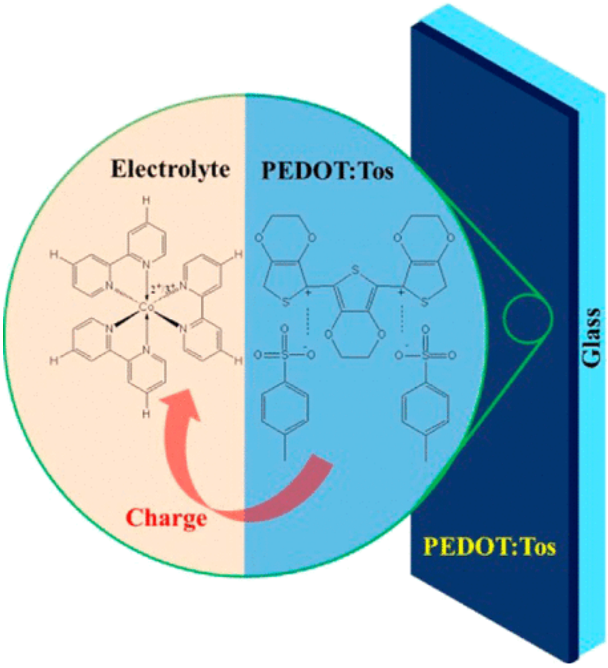

**FIGURE 17: ILLUSTRATION OF DYE SENSITIZED SOLAR CELLUSING POLY(3,4-ETHYLENEDIOXYTHIOPHENE) DOPED WITH IRON(III) TRIS-P-TOLUENESULFONATE,**
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CP can also be used for waste heat energy harvesting methodologies involving piezoelectric/ pyroelectric energy conversion. Talemi Pejman et al. fabricated a piezo/pyroelectric device where vapor phase polymerized (VPP) PEDOT was used as the flexible electrode overlay material and beta phase PVDF as the active material to create an all-polymer piezo/pyroelectric device. The change in normalized sheet resistance $R/R_o$ versus strain for the PEDOT-based electrodes was substantially lower than that of the platinum electrode, according to strain measurement up to the breaking-strain of PVDF (about 35%). Measurements of the contact angle revealed that a higher energy surface had formed, which allowed for a more adhesive interaction between the PVDF film and the PEDOT coating. This enhanced interaction between the two polymers resulted in a mechanical cam actuator producing a measured piezoelectric output voltage that rose from 0.2 V to 0.5 V under the same strain circumstances. By putting the film on and off of a hotplate, with temperatures up to 50˚C above ambient, pyroelectric open circuit voltage outputs of up to 100V and power outputs of up to 1 µW (into a 60 MΩ resistive load) were produced.[102]

In our work, we focused on pyroelectric energy conversion (PEC) which could make use of CP as electrode for it. We synthesized PPy flexible electrode using chemical oxidation method which was coated on PET substrate. Along with that, PVDF which has high beta phase crystallinity is also been used for this PEC. The PPy film shows a resistance of $60\ \Omega/cm^2$. The Fourier transform infrared spectroscopy (FTIR) in figure (18) shows that the band observed at 3227,2930,1655,1427,1070,923 $cm^{-1}$ corresponds to N-H stretch, $CH_2$ group, C=C stretch, PPy ring stretch, C-H wagging, C-H in plane. Further studies are to done for the usage of PPy as electrode. [unpublished]

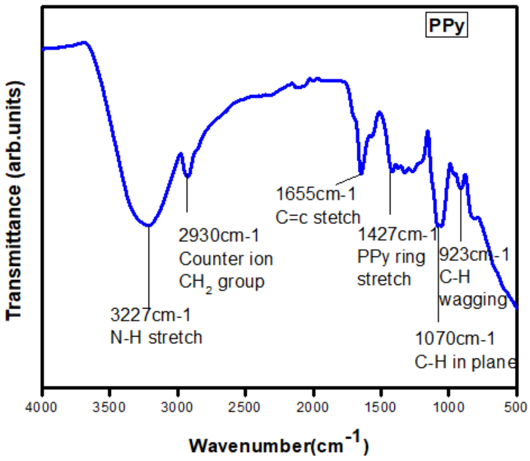

FIGURE 18: FTIR SPECTROSCOPY OF POLYPYRROLE.

## CONCLUSION

Numerous outstanding qualities that mirror those of metals are seen for conducting polymers (CPs). Hence it attracted the attention of the scientific community, however some of these features have been shown to be superior to those of metals in specific applications. However, research based on CP used as electrode materials for flexible devices are not much reported, which enables attention in the research field. Hence CP are in limelight with various applications.

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