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Synthesis of polyaniline and their application

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Abstract
One of the key new materials for the quickly advancing technology of PANI-based electronic devices, such as sensors, corrosion resistance, and radar absorbent materials, is polyaniline, or PANI. On the other hand, PANI is more difficult to work with than other common polymers and plastics. PANI is difficult to process because of its strong structure, which is a result of its high conjugation level. The development of PANI-based composites and blends is an alternate response to the difficulties encountered during the processing of neat PANI. This study focuses on the distinctive qualities and applications of the PANI processing research activities from 2003 to the present.

Keywords: Conducting polymer, PANI, synthesis, application

Introduction
The 1958 invention of polyacetylene marked the beginning of the era of inherently conducting polymers. However, due to its ease of synthesis and lower cost as compared to polyacetylene, polyaniline-commonly abbreviated as PANI or PAni-has garnered significantly greater attention from researchers. The history of PANI predates both polyacetylene and many other conducting polymers, even though the research of Alan G. McDiarmid, Hideki Shirakawa, and Alan J. Heeger is regarded as the groundbreaking work in the field of conducting polymers, for which they were awarded the Nobel Prize in 2000. Dr. Henry Letheby, a professor at the College of the London Hospital, initially reported the synthesis of "a blue substance" in 1862. This compound was created by electrolyzing aniline sulphate (AS), which partially decolorizes when exposed to a reducing agent. Because of its dark pigment colour, which was used to dye textile materials, it was known as "aniline black" in the past. Since then, a great deal of study has been done in this area to examine its possible applications in other fields. While dedoping doped PANI in the presence of a base degrades its electroactive properties, doping with acids improves electroactive behaviour. The extensive range of electrical and electrochemical properties of PANI, which may be tuned through doping or dedoping, along with its diverse range of nano- and microstructures, make it suitable for use in these fields. Applications such as fuel cells, gas sensors, pH sensors, and supercapacitors can benefit from PANI's reversible redox behaviour. PANI's frequency-dependent conductivity is used in the application of electromagnetic interference (EMI) shielding. Furthermore, a broad range of shapes, sizes, and crystal structures can be adjusted for PANI structures.

Among conducting polymers, polyaniline is the most promising and studied due to its high stability, high processability, and adjustable conducting and optical properties. Polyaniline's conductivity is reliant on the dopant concentration, and it only exhibits metal-like conductivity in pH values below 3 (Wang and Levon, 2012) [12]. There are various types of polyaniline (Fig. 1). Based on the degree of oxidation, they are categorized as leucoemeraldine, emeraldine, and pernigraniline; that is, leucoemeraldine is present in a state of adequate reduction, while pernigraniline is present in a state of complete oxidation. Only at a somewhat oxidised state does polyaniline become conductive; at a fully oxidised state, it behaves as an insulator (S. Bhandari, 2018) [31].

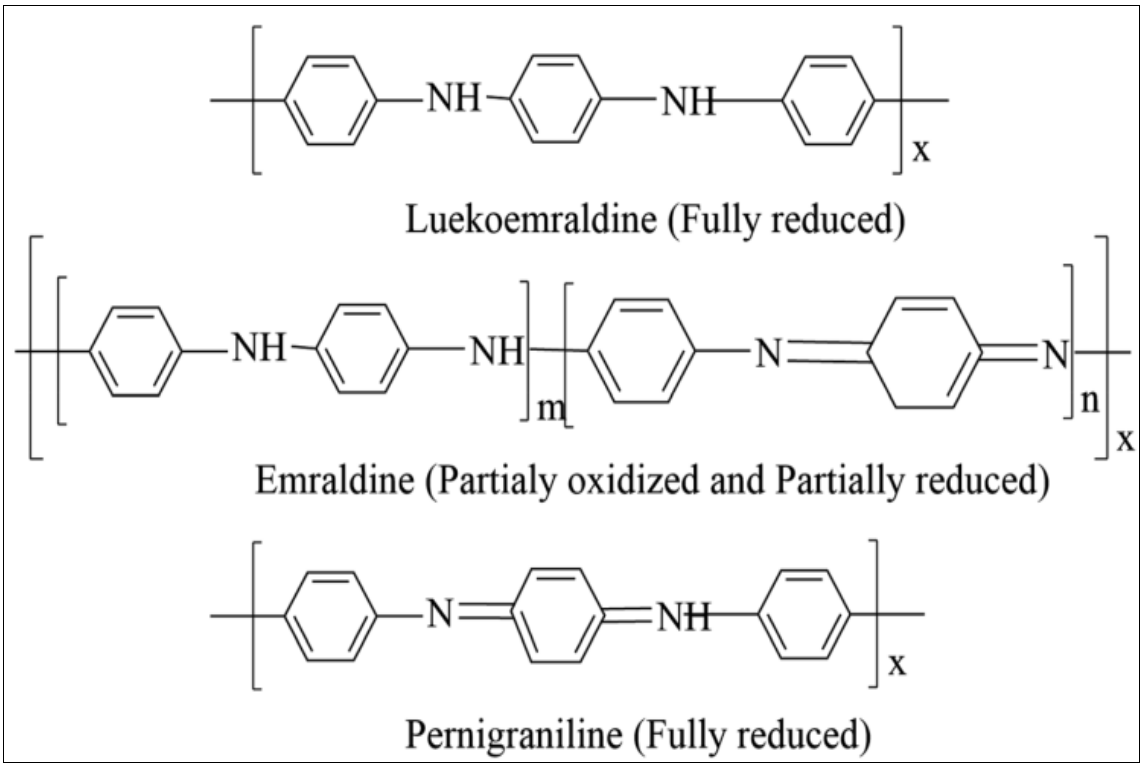

Fig 1: Numerous structural illustrations of different forms of polyaniline.

Different ratios of quinoid and benzoid rings make up the polymer backbone. The fully reduced leucoemeraldine form is in a quinoid state; the fully oxidised pernigraniline form is in a benzoid state; and the conductive emeraldine form has an equal ratio of both benzoid and quinoid rings. These three oxidised states are caused by differences in the ratio. The dopant is present in close proximity to the polymer chain and does not alter its chemical characteristics or form a link with it (Boeva and Sergeyev, 2014) [39]. This review has covered a broad summary of structures, attributes, and their connections.

Synthesis of Polyaniline

The reason PANI is regarded as an appealing electrically conductive polymer is its ability to be effortlessly transformed between base and salt forms by the addition of basic (OH^-) or acid (H^+). PANI was one of the most conductive polymeric materials the researchers worked with because of its resistance to oxidation and reduction, high electrical conductivity, simplicity in synthesis and modification, and durability in the environment. PANI was previously made via the oxidative polymerization of aniline monomers in an acidic media, but as PANI research and work progressed, other approaches and procedures were employed to make it, such as (Wallace *et al*., 2008) [11].

1. Electrochemical polymerization.
2. Chemical polymerization.
3. Vapor-phase polymerization (VPP).
4. Photochemically initiated polymerization.
5. Enzyme-catalyzed polymerization.
6. Polymerization employing electron acceptors.

Electrochemical Polymerization

Since many applications need for the manufacture of polymers in the form of a thin film with a large surface area, the electrochemical approach for creating conductive polymers is crucial to the process. PANI was prepared using electrochemical processes, utilising both galvanic and electrodynamic techniques. The process is carried out in a straightforward chamber cell with a power source, an electrode, and an electrolyte solution. The electrochemical method has numerous advantages over the chemical method, including being more affordable and simpler to use and producing a very pure and homogenous polymer deposited on the electrode (Beygisangchin *et al*., 2023) [40]. The following are the steps in the electro-polymerization procedure used to manufacture PANI: The suggested mechanism for the electro-polymerization of PANI (Fig. 2) is as follows: (1) formation of a positive free radical (cationic free radical) of aniline monomers by oxidation at the anode; (2) combination of the structures formed in the first step to form dimers through the process of removing protons and rearranging electrons in the aromatic rings; (3) growth of these formed dimers and the formation of new, larger structures; and (4) the last step is the spontaneous activation of the polymeric chain formed by the acid present in the solution to obtain the resulting denatured PANI.

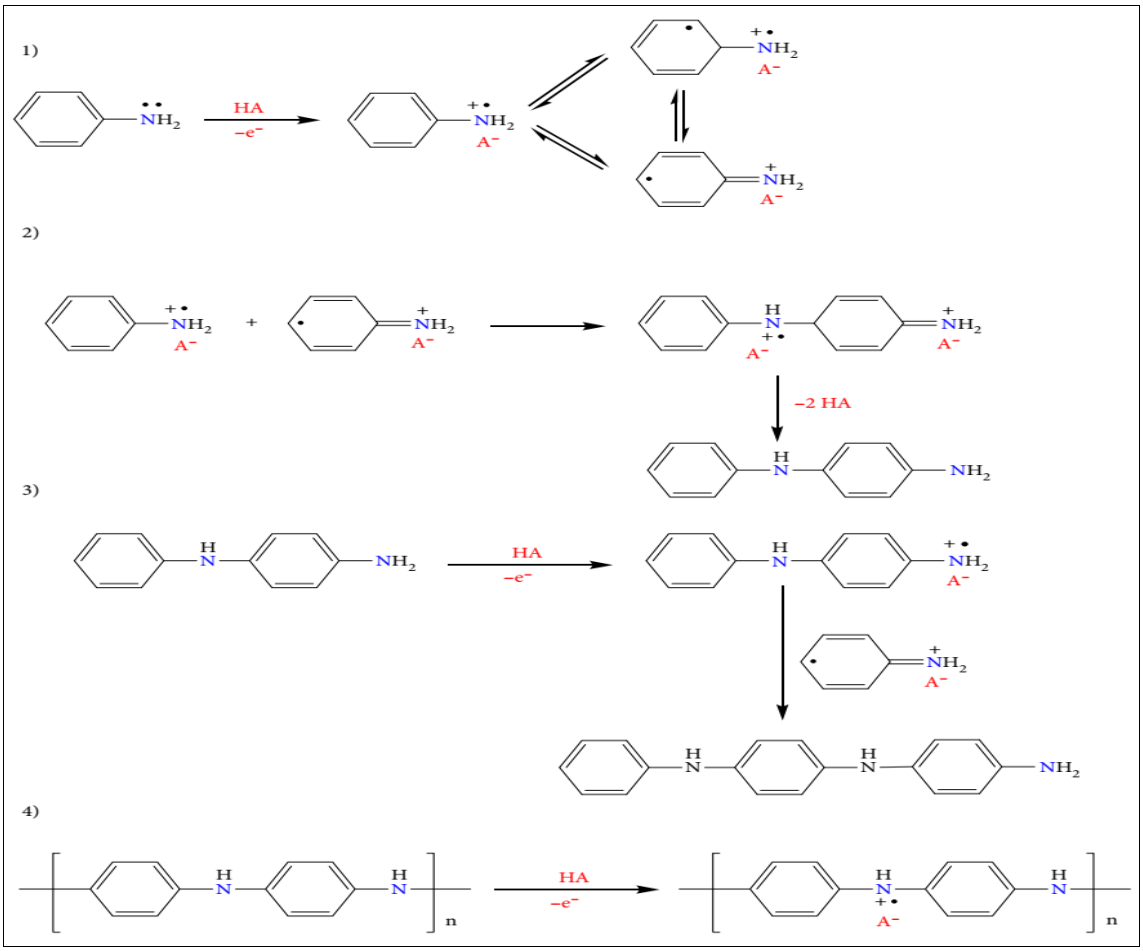

Fig 2: Proposal mechanism to form PANI using electrochemical polymerization.

In the case of polyacetylene, the electropolymerization process occurs without the assistance of an oxidant (AlMashrea *et al.*, 2020; Ashokkumar *et al.*, 2020) [6, 34]. Under the influence of a strong electrical field, electrospinning is also employed to synthesise fibrous polymer morphologies with nano- or micro-diameters. Here, a high voltage is delivered to the polymer droplets, causing the charged droplets to stretch as a result of surface tension. The liquid then erupts and begins to weave on the counter surface at a key point. Electrospinning and electrospraying work on the same principles. The sole technique available for creating large polymer fibrous structures is electrospinning. This method has been used to generate conducting polymers and their composites, such as pure polyaniline, polypyrrole, and polyaniline/polyethylene oxide/carbon nanotubes. Numerous variables affect electrospinning, including the polymer's molecular weight, viscosity, the distance between the spinneret and counter surface, temperature, humidity, and other variables (Cardenas *et al.*, 2007; Laforgue and Robitaille, 2008) [14, 4].

Chemical polymerization

One of the easiest ways to create polyaniline is by chemical oxidation; in this process, a monomer precursor of the corresponding polymer is combined with an oxidising agent in the presence of an appropriate acid in ambient conditions to produce products; the authors' preferred doping acid and oxidising agent are used in this process (Fig. 3). The synthesis of polyaniline is shown by the reaction media turning green. The same procedure is used for the preparation of the composite. Oxidising chemicals such as potassium bichromate, ceric nitrate, ammonium persulfate, ammonium peroxy disulfate, and so on are typically utilised. Effective modulation of the physical parameters by the conductivity is dependent on the pH of the acid dopant. When the pH is between 1 and 3, the polymer and composite have strong conductivity (Ravindrakumar, Bavane, 2014; Yang *et al.*, 2020) [15, 19].

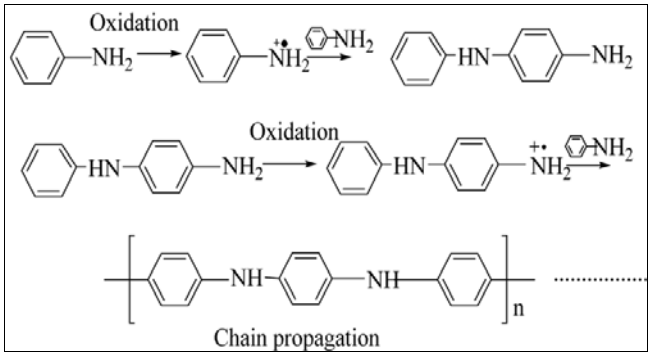

Fig 3: The chemical oxidation method of polyaniline synthesis.

Polyaniline is also made by interfacial polymerization, in which an aniline monomer is dissolved in an oxidant solution, an aqueous solution containing a dopant acid, and an organic solvent such as toluene. As an oxidant solution is introduced to the monomer solution, polymerization occurs in the interphase of these two immiscible liquids. The synthesis of polyaniline also employs a microemulsion approach; the only variation is in the surfactant employed. In this case, polymerization occurs at the interface between two immiscible liquids (Zeng *et al.*, 2015; El-Basaty *et al.*, 2020) [10, 1].

Vapor-Phase Polymerization

Vapor-Phase Polymerization (VPP) is one of the key steps in the synthesis of PANI. In 1998, conductive PANI was initially applied to cotton threads using this technique, which involved soaking the cotton threads in ammonium persulfate $(NH_4)_2S_2O_8$ and then using aniline steam to coat the cotton threads in conductive PANI (Das *et al*., 1998) [7]. Ultra-thin polymer films, including PANI, polypyrrole, polythiophene, and others, are produced with VPP technology. This procedure is a type of vapour phase self-assembly polymerization that can readily produce thin films of polymers with extremely high purity and superconductivity due to their lack of impurities and ability to be prepared at the nanoscale (Vellakkat *et al*., 2014; Meftah *et al*., 2014) [24, 5].

Photochemically Initiated Polymerization

A viable and alluring technique for creating PANI with distinctive characteristics and compositions is photocatalytic polymerization. Furthermore, it's a crucial process for creating hybrid materials (Zarrintaj and Saeb, 2019) [29]. Kobayashi and colleagues showed in 1998 (Teshima *et al*., 1998) [16] and 2001 (Kim *et al*., 2001) [37] that PANI can be produced by photopolymerization using single- or bi-layer films that contain methylviologen (MV^{2+}) as an oxidant and [Ru $(bipy)_3]^{2+}$ as a primer. The films are then exposed to visible light to yield PANI. When [Ru $(bipy)_3]^{2+}$ is exposed to radiation at 452 nm, the triple excited state *[Ru $(bipy)_3]^{2+}$ is produced. The powerful oxidant [Ru $(bipy)_3]^{3+}$ is produced as a result of the electron transfer process between *[Ru(bipy)3] 2+ and MV2+. This process oxidises aniline and then polymerizes it to form PANI. For usage in molecular electronics later on, the generated PANI was deposited in these investigations onto monolayer or bilayer films. Subsequently, a variety of methods, such as gamma rays (Hamdi-Mohammadabad *et al*., 2021), microwaves (Gizdavic-Nikolaidis *et al*., 2010) [23], ultraviolet rays (Sury *et al*., 2021) [35], and X-rays (Felix *et al*., 2011) [13], were employed for the irradiation process to create PANI using an external source.

Enzyme-Catalyzed Polymerization

In previous years, scientists have turned to employing enzymes, such horseradish peroxidase (HRP), as catalysts to synthesise significant polymers, like poly pyrrole and PANI, when oxidants, like peroxide, are present (Jabłońska *et al*., 2015) [2]. Since the peroxide is transformed into water, this process is thought to be environmentally benign; yet, numerous investigations have resulted in low molecular weight branching polymers. In order to get around these issues, Samuelson *et al*. (1998) [17] produced regular polymeric chains in the HRP-catalyzed PANI production mixture by using other electrolytes, such as poly (styrene sulfonate) (PSS), as templates. In this procedure, PSS has three responsibilities to play: (i) Before beginning the polymerization process, PSS serves as a template to align the aniline monomers in the correct head-to-tail coupling orientation. (ii) It offers crucial doping for the activation of PANI, resulting in the formation of electrically conducting emeraldine salt. (iii) It gives the (PAni/PSS) product its water solubility. Using this approach, water-soluble PANI is produced by polymerization in an acidic medium with a pH of 4. According to Nagarajan *et al*. (2001) [30], DNA and poly (vinylphosphonic acid) are suitable electrolytes that are employed.

Application of Polyaniline

Since their creation, conductive polymers have demonstrated incredibly unusual qualities because of their unique electronic configuration, chemical makeup, and variety of physical characteristics. As a result, they are vital components of numerous applications. For instance, PANI is a good electrical conductive polymer that is attracting the attention of many researchers for its usage in various applications because of its low cost, ease of manufacturing, unique features, and nonpolluting nature. The following are the most significant applications where PANI is utilised either as a primary or secondary material.

Supercapacitor

Gas, natural gas, and fossil fuels are only a few examples of the various energy sources that are used, and their use has been greatly influenced by the global economy. Although using this fuel produces clean energy, it also has a negative impact on the environment. To address this, scientists have long worked to create high-energy, renewable, and ecologically acceptable energy sources like fuel cells, supercapacitors, water energy, and wind energy. Because they are employed in so many various applications, including wearable technology and electrical and electronic devices, super capacitors are regarded as one of the most promising energies and will have significant commercial value in the future markets (Meng *et al*., 2013) [8]. PANI is a material that works well in supercapacitors due to its many oxidation states, high conductivity, and specific capacitance. The characteristics of PANI, such as its production technique, chemical and physical properties, dopant, and nanostructure, affect the electrochemical properties of supercapacitors in which it is utilised as a base material in the electrodes (Wang *et al*., 2012) [12]. The supercapacitors were created by combining PANI with a variety of carbon molecules, including graphene oxide, graphene, fullerene, and carbon nanotubes (Bandyopadhyay *et al*., 2017; Zhang *et al*., 2020) [27, 25]. For the same objective, metal nanoparticles containing PANI were also employed (Li *et al*., 2015; Rantho *et al*., 2020) [9, 22].

Sensors

A sensor is a gadget that can identify changes in its surroundings and indicate when other objects are present. Nowadays, organic or inorganic semiconducting materials or films make up most prevalent sensors (Kreno *et al*., 2012) [18]. Among these polymers is PANI, which has drawn a lot of attention as a sensor because of the various morphologies and configurations it can be manufactured in, including microstructures, nanowires, nanotubes, nanoparticles, and nanosheets (Abd Razak *et al*., 2015) [33]. Chemical and biological sensors, among others, have been produced using PANI or one of its nanocomposites. Because of their extremely large surface area and potential for gas emission, researchers have attempted to create PANI with a variety of nanostructures, including nanofibers, nanowires, and nanotubes. These nanostructures have subsequently been employed in gas sensors. Gold nanoparticles are grafted with PANI to form gold nanocomposites with PANI, and this new system can easily detect H_2S gas, with the response rate reaching very low concentrations (0.1 ppb). Pure PANI cannot detect H_2S gas alone because H_2S gas molecules cannot change the conductivity of PANI (Shirsat *et al*., 2009) [21].

A discernible structural alteration in the PANI nanostructure chains resulted from the application of PANI nanostructures to detect the presence of ammonia, hydrochloric acid, hydrazine, chloroform, carbon oxides, and methanol (Virji *et al*., 2004) [36]. By combining several nanomaterials to create PANI nanocomposites, one can enhance PANI's sensing capabilities. This can shorten the sensing duration and enable the detection of materials or gases at extremely low concentrations (Pawar *et al*., 2012; Liu *et al*., 2015; Liu *et al*., 2020) [32, 10, 26].

Conclusions

The focus of all current research is on providing polymeric composites containing metals or their oxides in addition to different types of composites to enhance certain qualities. PANI has always drawn interest from academics in their studies and in a variety of applications, the most significant of which is electrical applications, due to its original unique electrical properties. During this investigation, we came to the conclusion that PANI's electrical characteristics may be enhanced for usage in sensor applications and other uses. During this study, we came to the conclusion that PANI's properties can be enhanced by grafting it with other materials, particularly nanomaterials, to create polymeric nanocomposites of PANI. These can then be used to enhance the applied properties of supercapacitors, gas sensors, and other devices, as this study has shown.

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