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Polyaniline nanomaterials: Structure, preparation and application

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Abstract
Popular conductive polymer polyaniline (PANI) has drawn a lot of attention from nanotechnology researchers who hope to use it to enhance sensors, optoelectronics, and photonics. PANI is easily doped with various acids and dopants due to its exceptional environmental stability and ease of production. This review focuses on the many chemical and physical procedures used to create PANI thin films. This review covers a number of PANI thin film characteristics, including their electrical and sensing, anti-corrosion, redox, antioxidant, and magnetic qualities. One very conductive polymer is PANI. It has drawn a lot of attention because of its special qualities, ease of synthesis, affordability, and high environmental stability in a variety of applications, including electronics, medications, and anti-corrosion materials. At the conclusion of this review, the most significant PANI applications are briefly discussed.

Keywords: Polyaniline, synthesis, applications, sensors, drug delivery, solar cell

Introduction
Depending on its degree of oxidation, polyaniline (PANI), formerly known as black aniline, can take on several forms. In addition, PANI is well-known for its environmental stability, doping potential with protonic acids, and simplicity (Bhadra *et al*., 2020; Park *et al*., 2016) [1, 7]. By linking the 1, 4-coupling of the aniline monomer components, PANI can be found. PANI can be identified using FTIR benzenoid to quinonoid ratios, and it may exist in many oxidation states.

Polyaniline (PANI), polythiophene (PTH), polypyrrole (PPY), and their byproducts are the main types of conjugated conductive polymers (Gómez *et al*., 2021) [14]. According to Liao (2018) [10], they have a wide range of possible uses, including microwave absorption, gas separation membrane, chemical sensor, rechargeable battery, photovoltaic cell, electromagnetic interference shielding, and photothermal therapy. These substances have potential uses in electronic devices, shields against electromagnetic interference, and electrodes for displays (Al-Oqla *et al*., 2015; Sobha *et al*., 2017) [9, 4]. For instance, PANI's low processing capacity, rigidity, and lack of biodegradability limit its biological applications. According to Kenry and Liu (2018) [22], the primary issue with PANI is its poor solubility, which is impacted by its stiff spine. Numerous techniques have been tried to increase its processability; two significant attempts to get beyond these drawbacks are chemical alterations, including the use of doped PANI and substitute PANI derivatives.

Generally speaking, it is thought that one possible way to enhance the characteristics and functionality of PANI is to construct PANI-based compounds using both organic and inorganic nanofillers. Materials produced using these methods combine PANI with organic and inorganic nanoparticles in ways that are complimentary or synergistic. Intrinsically conducting polymers are organic polymers that exhibit the electrical, optical, and magnetic properties of metals; these polymers are electroactive and have the aforementioned behaviours while preserving their structural characteristics. These polymers exhibit good electrical conductivity without the need for conductive additives because of conjugated double bonds in their backbones. In a doped condition, they transform to high conductivity on their own. Through the doping method, which uses both N-type (electron donors) and P-type (accepting electrons) dopants to induce an insulator-to-metal transition in electronic polymers, the conductivity of the polymers is increased to a metallic state from their insulating state (Heeger *et al*., 1988) [2]. It was demonstrated that by adding acidic or basic solutions during polymerization or post-processing, it may be chemically or electrochemically added to or removed from the polymer chain.

The resulting positive (hole) or negative (electron) ions are free to move throughout the polymer chain during this process. To generate materials with the synergistic impact of both PANI and inorganic nanoparticles, many forms of PANI composites with inorganic nanoparticles, such as CeO_2, TiO_2, ZrO_2, Fe_2O_3, and Fe_3O_4, have been described (Aphesteguy and Jacobo, 2007) [16]. According to Prabhakar *et al*. (2011) [32], these composites find application in a multitude of sectors, including electrochromic devices, LEDs, EMI shielding, electrostatic discharge systems, batteries, and chemical and biological sensors. PANI is present in one of the three idealised oxidation states—leucoemeraldine (white/clear), emeraldine (salt-green/baseblue), or pernigraniline (blue/violet)—during the polymerization of aniline monomer (Fig. 1). It has multiple uses, including gas separation membranes (Beygisangchin *et al*., 2021) [25], chemical sensors (Stamenov *et al*., 2012) [34], and solar cells. PANI microtubes/nanofiber, PANI-multi-walled carbon nanotubes (Wang *et al*., 2019) [41], and nanocomposites are employed as microwave safeguards and electromagnetic shielding materials (Saini *et al*., 2009) [33] in addition to all the other uses mentioned above.

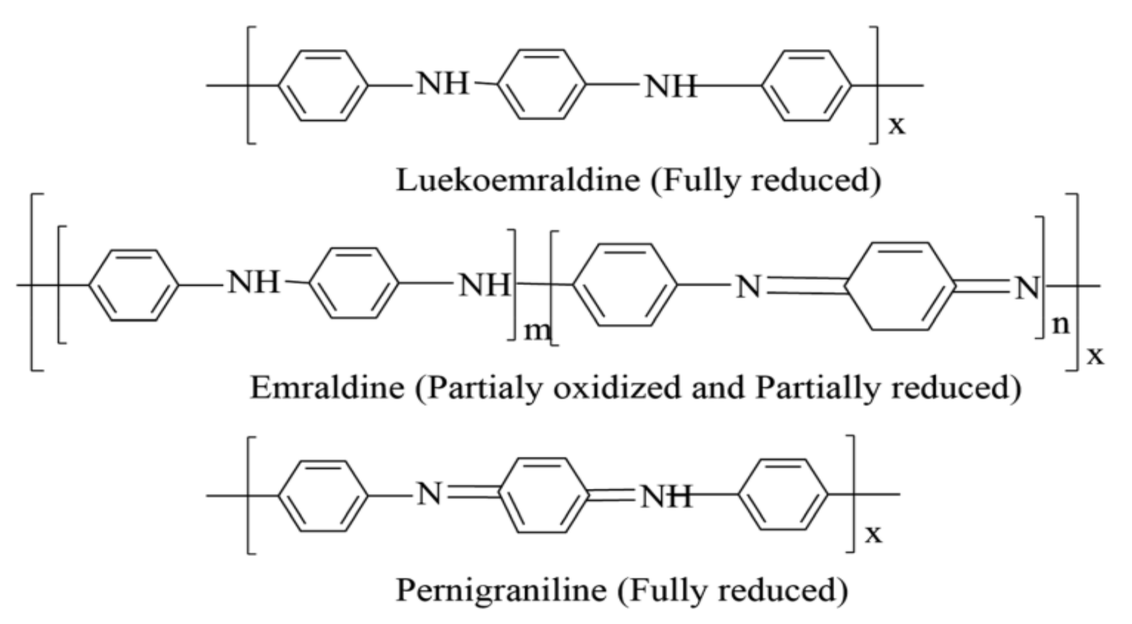

Fig 1: Numerous structural illustrations of different forms of polyaniline (DOI: 10.1039/d0ra07800j, RSC Advances).

In order to create a close connection between PANI chemical alterations and real-world applications, this study primarily focuses on advancements in PANI chemical modification and enhanced characteristics during the previous few decades. To set the stage for further research, the paper also discusses the various approaches used to prepare PANI and PANI thin films.

Synthesis of PANI

In recent studies, there have been numerous reports for the oxidative polymerization technique of PANI preparation. In this technique, polymerization and doping occur simultaneously with chemical or electrochemical methods.

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) [20, 3].

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. 2). 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) [21, 23].

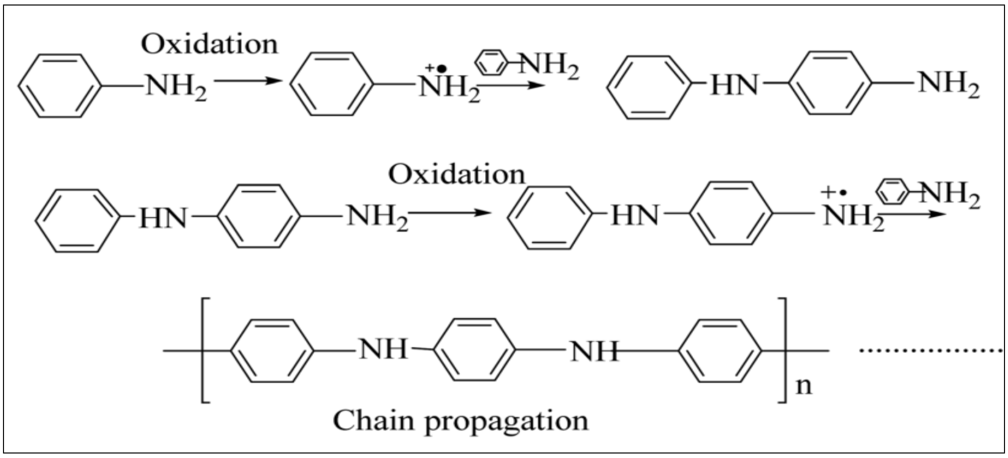

Fig 2: The chemical oxidation method of polyaniline synthesis.

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) [45, 1].

PANI Applications

By virtue of their inherent electrical activity, conductive polymers offer special qualities that have led to a wide range of uses. PANI is a highly conductive polymer that is gaining significant attention in a variety of applications due to its low cost, distinctive characteristics, and ease of manufacturing (Fig. 3).

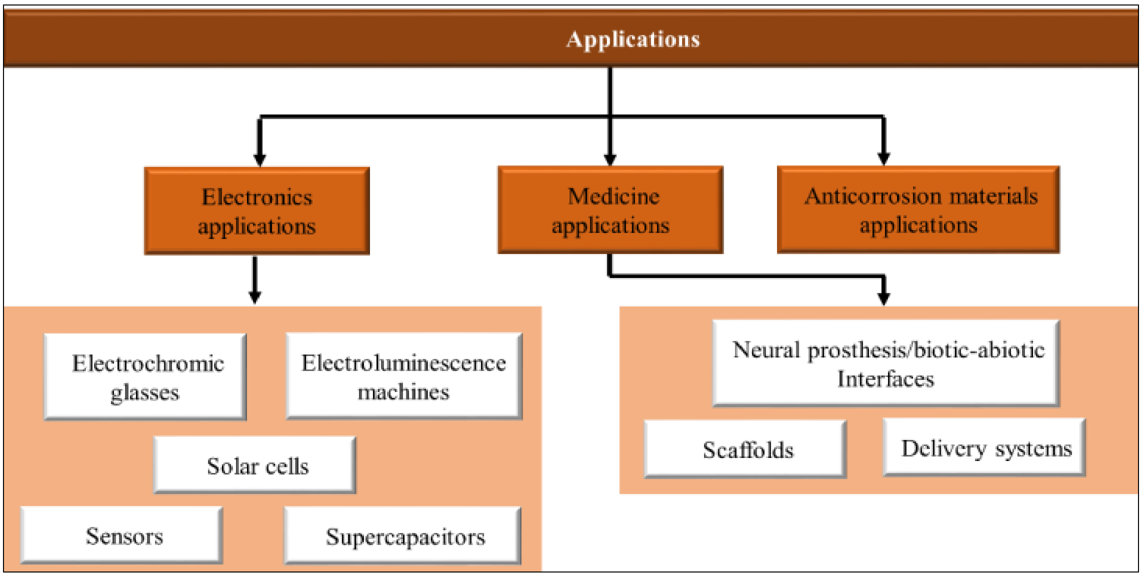

Fig 3: Numerous applications of PANI

Electrochromic Glasses

If an electric current flows through smart or electrochromic glass, it will change colour. The grade of voltage transfer across an electrochromic glass will dictate the glass's level of turbidity. Intelligent material's oxidation or reduction state is visible to the unaided eye. Among these materials is PANI, which has the ability to reflect blue light, much like a crystal medium in an electric current tunnel. Glass has many modes, colours, and translucencies when it comes to opacity (Yang and Mai, 2015) [35]. The creation of technologies having both internal and external applications is facilitated by this attribute. For instance, an electric current can be used to change the darkness of a car window over a wide range of potentials; similarly, antiquities in a museum's exhibition hall are protected from UV rays and artificial light (Zarrintaj *et al.*, 2019) [37]. According to several studies (Tavares *et al.*, 2014; Yang and Mai, 2015; Silva *et al.*, 2016; Chu *et al.*, 2018; Lyu *et al.*, 2020) [36, 35, 13, 17], discolouration in electrochromic glass is dependent on the electric current of the chains.

Electroluminescence Machines

Electroluminescence devices can be produced from materials that release light when an electric field or current is introduced. These are light-emitting diodes (LEDs) of a p-n connection diode that, when the right voltage is applied, can produce radiation. Thus, photon energy can be released by combining electrons with the electron holes in the device (Jang *et al.*, 2008) [18]. LEDs are built using PANI electro-luminescence structures (Liu *et al.*, 2013) [19].

Solar cells

PANI has also encouraged the commercial application of low-cost solar cell fabrication technologies for solar cells (Xiao *et al*., 2014) [42]. PAN-based solar cells improve energy efficiency while lowering the cost of invention. Based on an electrolyte and a semiconductor, dye-sensitive solar cells (DSSCs) are low-cost, high-performance film solar cells (Hosseinnezhad *et al*., 2017a, b, c) [26, 27, 28].

Sensors

PANI's various architectures and morphologies, including nanowires, have garnered significant interest for it as a sensor (Tahir *et al*., 2005) [44]. PANI will manufacture a variety of precision sensors, including chemical and biological sensors (Dhand *et al*., 2011) [5]. Because of PANI's exceptional surface area and potential for gas emission, researchers have attempted to utilise it in gas sensors with a variety of nanostructures, including nanofibers, nanowires, and nanotubes. Thus, PANI-based sensors-such as gas and glucose sensors-are developed for diagnostic applications (Ramanavicius and Ramanavicius, 2021) [40].

Supercapacitor

According to Meng *et al*. (2013) [6], super capacitors are considered one of the most promising energy sources and will have a substantial commercial value in the future due to their wide range of applications, which include wearable technology and electrical and electronic equipment. 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) [11]. 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) [31, 30]. For the same objective, metal nanoparticles containing PANI were also employed (Rantho *et al*., 2020) [29].

Medical Applications

One of the most well-known ICPs, PANI, has a wide range of possible uses in biomedicine because of its hydrophilic environment, low toxicity, high environmental stability, and nanostructured shape, which all contribute to its excellent electrical conductivity and biocompatibility. The most recent biological activities and uses of PANI-based nanocomposites in the medical domains, including neural prosthesis/biotic-abiotic interfaces, scaffolds, and delivery systems, are described in this review (Zare *et al*., 2020) [8]. Medicine today is primarily an engineering field, and new intellectual technologies are needed to improve this field. Devices that compensate for nerve weakening and advance neuroscience are necessary for neuroscientists (Asplund *et al*., 2014) [24]. Biocompatibility conductive scaffolding has high bio-counterfeit qualities, and it has been used to treat organ problems (Dong *et al*., 2015; Atoufi *et al*., 2017) [39, 43]. Furthermore, PANI applications have drawn a lot of interest in delivery systems, which has led to the exploration of novel delivery structures such electro-drug delivery systems (Dong *et al*., 2016) [38].

Conclusion

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. Recent findings about the chemistry of PANI have motivated scientists to focus their attention on this area of study. It seemed to PANI to have key characteristics that set it apart from the other polymers. PANI's electrical conductivity is one of its most significant qualities, and its range of uses has allowed researchers to explore new areas in this area. It was discovered that PANI has actual electrical qualities that make it a key component of numerous applications that could greatly benefit humanity, such as fuel cells, solar cells, super capacitors, various sensors, and batteries of all kinds. It was also discovered that grafting PANI with certain nanomaterials to create PANI nanocomposites greatly enhances its electrical characteristics. 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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