

Synthesis and applications of Polyaniline: A Brief Review

*^{1,2}Satish S. Haral, ³Umesh J. Tupe, ²Vijay S. Kale,

¹MVP's KANMS Art's, Commerce and Science College Satana, Nashik, Affiliated to Savitribai Phule Pune University, Maharashtra, India

²Department of Electronic Science and Research Centre, MGV's L.V.H. ASC College, Nashik, Dist.-Nashik, affiliated to Savitribai Phule Pune University, Maharashtra, India

³Department of Electronic Science, Vidya-Amrut Dnyan Pratishthan's Arts, Science and Commerce College, Shirsondi, Tal- Malegaon, Dist. Nashik, Affiliated to Savitribai Phule Pune University, Maharashtra, India

Corresponding author: hrlsatish@gmail.com

Abstract: Polyaniline (PANI), an electrically conducting polymer and organic semiconductor, belongs to a group of semi-flexible rod polymers. Because of this polymer's well-known conductive characteristics, scientists studying nanotechnology are very interested in using it to improve photonics, optics, and sensors. It's also thought of as being one of the conductive polymers that's used as an anticorrosion coating the most. PANI has demonstrated significant promise as an electrode for supercapacitors because of its many benefits, including low cost, strong electrical conductivity, many redox states, and sustainability. PANI is easy to produce and has remarkable stability in the environment. The primary focus of the present review paper is to provide information on the different synthesis methods and applications of PANI. This review paper also explores the future perspectives of polyaniline.

Keywords: Polyaniline, polymers, electrical conductivity, synthesis methods, supercapacitors.

1. Introduction:

Polyaniline is a conducting polymer that has gained significant attention in the field of materials science due to its unique properties and various potential applications. Polyaniline exhibits both metallic and semiconducting behavior, depending on the dopant and its oxidation state [1, 2]. It can have high conductivity in its doped form. It is stable in air and can withstand exposure to moisture and chemicals, which makes it suitable for various applications. It can be easily processed into different forms such as films, fibers, and nanoparticles, enabling its use in flexible electronics, coatings, and composite materials. PANI is a lightweight and flexible material, which makes it suitable for applications requiring flexibility, such as wearable electronics and sensors [2-4]. It has great electrical conductivity in the range of 10^{-10} to 10^2 S/cm. It has band gaps of 4.3 and 2.7 eV in its reduced and oxidized forms respectively. It has high chemical stability. Polyaniline exhibits a relatively small bandgap, making it a semiconductor material. It has a relatively high dielectric constant (~20-30), indicating its ability to store electrical energy in an electric field. The bandgap determines the energy required to excite electrons from the valence band to the conduction band, and thus influences the electrical conductivity and optical properties of the material [4, 5]. The properties of polyaniline are tunable hence it is used in many applications. The properties such as electrical conductivity and optical properties can be tuned by controlling the synthesis conditions and dopants used. Polyaniline is synthesized by various methods; the most common method for synthesizing polyaniline is through chemical oxidation of aniline monomers using oxidizing agents such as ammonium persulfate or ferric chloride. Polyaniline can be synthesized by using templates such as micelles or nanoscale structures, which result in the formation of polyaniline with specific morphologies, such as nanofibers or nanoparticles according to review. It is also synthesized electrochemically using aniline as the monomer and an electrolyte solution as the dopant source [6, 7]. This method offers precise control over the polymerization process. There are many applications of PANI including conductive coatings, energy storage, sensors, flexible electronics devices, anticorrosive coatings and supercapacitors. Polyaniline can be used as an electrically conductive coating in various applications, such as antistatic coatings, electromagnetic shielding, and corrosion protection. It has been explored for use in batteries, supercapacitors, and energy storage devices due to its high conductivity and charge storage capabilities [7-9]. The structure of polyaniline is illustrated in Fig. 1. Polyaniline-based sensors are used for detecting gases, chemicals, humidity, and strain, making them useful in environmental monitoring, industrial applications, and healthcare. Polyaniline's lightweight, flexible nature makes it suitable for applications in flexible electronics, such as flexible batteries, electronic displays, and wearable electronics [11, 12]. It has shown promise in drug delivery systems, tissue engineering, and biosensing applications due to its

biocompatibility and tunable properties. Polyaniline coatings have been used to protect metals from corrosion by providing a barrier against moisture and chemicals. These are just a few examples of the many potential applications of polyaniline, and ongoing research continues to explore its use in various fields. The present review article discussed in the brief the different synthesis methods and applications of polyaniline.

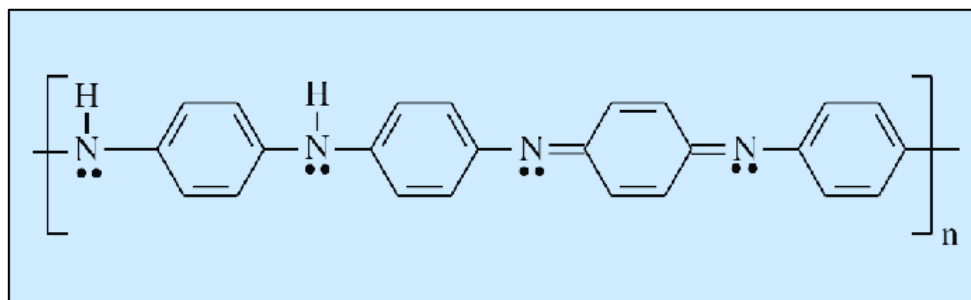


Figure 1: Structure of polyaniline

2. Literature review:

Polyaniline was first synthesized in 1981 by Japanese scientist Hideki Shirakawa and his team. They accidentally discovered its conductive properties while attempting to synthesize a compound related to acetylene. Shirakawa, along with Alan MacDiarmid and Alan Heeger, was awarded the Nobel Prize in Chemistry in 2000 for the discovery and development of conducting polymers, including polyaniline. In front of the investigators, a brand-new, unique conducting polymer, polymerization process, and electron transport mechanism progressively evolved after that [13, 14]. Numerous conducting polymers, including polythiophene, polypyrrole, polyaniline, and polycarbazole, were developed following polyacetylene, the first conducting polymer to be synthesized. Polyaniline is one of the most often documented conducting polymer among these, having found uses in optical electronics, photovoltaic cells, supercapacitors, and anticorrosion materials [9-13].

Tang, Z., et al. [14] synthesised polyaniline nanoparticles using a pulsed potentiostatic technique. Polyaniline nanoparticles were synthesized from a dilute polyaniline acidic solution (1 mM aniline+1 M HClO₄) on a highly oriented pyrolytic graphite surface. According to FT-IR-ERS and XPS data, the polyaniline was in its emeraldine form. Based on the TMAFM measurement, the electropolymerized polyaniline nanoparticles covered approximately 1010 cm⁻² on the HOPG surface. It is observed that the surface concentration and size of these nanoparticles varied over a large range by changing the charge of electropolymerization. The disk-shaped nanoparticles had an apparent diameter ranging from 200 to 600 Å and a height between 10 and 30 Å. Particle size rose from 5.7 to 19.3 μC cm⁻² as the electro polymerization charge increased. Kinyanjui, J.M., et al. [15] synthesised polyaniline/platinum composites (PANI/Pt) using both chemical and electrochemical methods. In accordance to the authors, aniline is oxidized by PtCl₆²⁻ in the absence of a secondary oxidant, which results in the direct chemical synthesis of PANI/Pt. PtCl₆²⁻ is taken up and reduced into an a priori electrochemically formed PANI sheet to start the electrochemical PANI/Pt synthesis. The findings suggest that regulating particle dimension might be better accomplished via electrochemical techniques. The reduced proton doping in both materials when compared to PANI without Pt suggests that the metal particles have a direct impact on the polymer's oxidation state and proton doping. According to the electrochemical data, PANI/Pt made by any synthetic approach can achieve the normal acid doping since there is enough conductivity in the solution. Chiral PCA was used as a template by Yang et al. [16] for producing chiral PANI nanotubes with an aspect ratio of 6–10, an outer diameter of 80–220 nm, and an inner diameter of 50–130 nm. PANI nanofibers were generated by Li et al. [17] using p-aminobenzenesulfonic acid as the surfactant. The nanofibers had lengths of several micrometers and diameters of 100–120 nm. As the concentration of p-aminobenzenesulfonic acid declined, so did the diameters of the nanofibers. Yang et al. [18], worked on self-doping monomer o-aminobenzenesulfonic acid was used as the surfactant to make self-doped PANI nanofibers with a diameter range from 120 to 370 nm.

3. Synthesis methods of Polyaniline:

Polyaniline is synthesized through various methods, including chemical, physical, chemical oxidation, electrochemical polymerization, and template-assisted synthesis methods [19-22]. The Fig. 2 shows that the methods implanted for the synthesis of polyaniline.

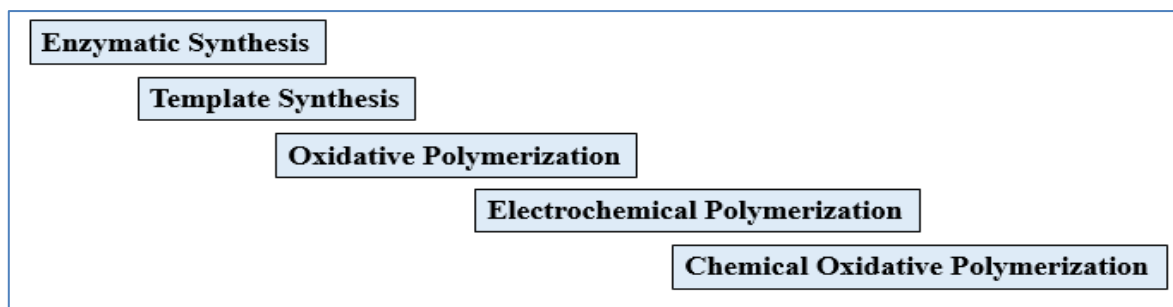


Figure 2: Synthesis methods of polyaniline

1. **Oxidative Polymerization:** In this method, aniline monomers are oxidized in the presence of an oxidizing agent such as ammonium persulfate, ferric chloride, or hydrogen peroxide. The reaction is typically carried out in an acidic medium, such as hydrochloric acid or sulfuric acid, to facilitate the formation of the polymer. The resulting polyaniline can be in the form of emeraldine salt, which can be converted to its conductive form, emeraldine base, through dedoping.
2. **Chemical Oxidative Polymerization:** This method involves the chemical oxidation of aniline monomers using various oxidizing agents, such as ammonium persulfate, ferric chloride, or potassium dichromate. The reaction is generally carried out in an acidic solution at a controlled temperature to regulate the polymerization process and the properties of the resulting polyaniline.
3. **Electrochemical Polymerization:** In electrochemical polymerization, aniline monomers are polymerized on the surface of an electrode in the presence of an electrolyte and an applied potential. This method allows for better control over the polymerization process and can yield polyaniline with specific properties tailored to the application.
4. **Template Synthesis:** Template synthesis involves the use of a template or a matrix to guide the polymerization of aniline monomers, resulting in the formation of polyaniline with a defined structure. Templates can include porous materials, zeolites, or other polymers, and the method can provide control over the morphology and properties of the resulting polyaniline.
5. **Enzymatic Synthesis:** Enzymatic synthesis of polyaniline involves the use of enzymes to catalyze the polymerization of aniline, offering an environmentally friendly and potentially more controlled approach to synthesizing polyaniline.

4. Applications of Polyaniline:

Polyaniline is a versatile conducting polymer, and it employ in various fields due to its unique properties [21-25]. Few of the applications of polyaniline are listed below-

4.1 Antistatic Coatings: Polyaniline is used in antistatic coatings for materials like textiles, plastics, and electronics to prevent static electricity buildup. These coatings are essential in industries where static electricity can damage sensitive electronic components or cause hazards in explosive environments.

4.2 Corrosion Protection: Polyaniline can act as a corrosion inhibitor for metals, providing protection against corrosion in harsh environments. Coatings containing polyaniline can be applied to metal surfaces to extend their lifespan and prevent degradation due to corrosion.

4.3 Sensors: Polyaniline-based sensors are widely used for detecting gases, humidity, and chemical analytes. The conductivity of polyaniline can change in response to the presence of specific gases or chemicals, making it suitable for sensing applications. Polyaniline sensors are used in environmental monitoring, industrial safety, and healthcare diagnostics.

4.4 Batteries and Supercapacitors: Polyaniline exhibits high electrical conductivity and can store electrical charge, making it a promising material for batteries and supercapacitors. Research is ongoing to develop polyaniline-based electrodes for energy storage devices with improved performance, including high energy density and fast charge/discharge rates.

4.5 Electronic Devices: Polyaniline can be incorporated into electronic devices such as organic light-emitting diodes (OLEDs), organic field-effect transistors (OFETs), and organic photovoltaic cells (OPVs). Its semiconducting properties make it suitable for use in flexible and lightweight electronic devices, including displays, sensors, and photovoltaic modules.

4.6 Smart Textiles: Polyaniline-coated textiles can exhibit conductive properties, allowing for the integration of electronic functionalities into clothing and fabrics. Smart textiles incorporating polyaniline can be used for applications such as wearable electronics, biomedical monitoring, and military uniforms with embedded sensors for monitoring vital signs or environmental conditions.

4.7 Water Purification: Polyaniline-based materials have been explored for water purification applications, including the removal of heavy metals and organic pollutants from contaminated water. Polyaniline composites with other

materials, such as nanoparticles or activated carbon, can enhance their adsorption capacity and efficiency in water treatment processes.

4.8 Biomedical applications: Polyaniline has potential applications in biomedical engineering, including drug delivery systems, tissue engineering scaffolds, and biosensors for detecting biomolecules. Its biocompatibility, tunable properties, and ability to respond to external stimuli make it a promising candidate for various biomedical applications.

4.9 Conductive Polymers: Polyaniline is used as a model system for studying the fundamental properties of conducting polymers and exploring potential technological applications.

5. Future perspectives of polyaniline

The future perspectives of polyaniline are promising, with ongoing research aimed at addressing its limitations and expanding its applications. The future of polyaniline looks bright, with exciting opportunities for innovation and applications across diverse fields such as electronics, energy, environment, and healthcare. Continued research and collaboration between academia, industry, and government organizations will play a crucial role in unlocking the full potential of polyaniline for advanced technologies and sustainable solutions.

5.1 Improved Synthesis Methods: Researchers are continuously exploring new synthesis routes and processing techniques to improve the properties and performance of polyaniline. Innovative approaches, such as template-assisted synthesis, electrochemical polymerization, and green chemistry methods, can lead to the production of polyaniline with enhanced conductivity, stability, and processability.

5.2 Composite Materials: Polyaniline can be combined with other materials, such as carbon nanotubes, graphene, metal oxides, and polymers, to form composite materials with synergistic properties. These composite materials can exhibit improved conductivity, mechanical strength, and chemical stability, enabling new applications in energy storage, sensors, catalysis, and biomedical devices.

5.3 Energy Storage Devices: Polyaniline-based electrodes for batteries, supercapacitors, and hybrid energy storage systems hold great promise for the development of high-performance energy storage devices. Future research aims to optimize the electrode structure, doping level, and electrolyte compatibility to achieve higher energy density, faster charging rates, and longer cycle life.

5.4 Flexible and Wearable Electronics: Polyaniline's flexibility, lightweight, and conductivity make it an ideal candidate for flexible and wearable electronics. Future developments may include the integration of polyaniline-based conductive inks, films, and coatings into wearable sensors, displays, and electronic textiles for applications in healthcare, sports monitoring, and human-computer interaction.

5.5 Environmental Remediation: Polyaniline-based materials can be used for environmental remediation applications, such as water purification, air filtration, and soil remediation. Future research may focus on the development of polyaniline-based adsorbents, membranes, and catalysts for the removal of pollutants, heavy metals, and organic contaminants from the environment.

5.6 Biomedical Engineering: Polyaniline's biocompatibility, tunable properties, and stimuli-responsive behavior make it a promising material for biomedical applications. Future research may explore the use of polyaniline-based materials for drug delivery systems, tissue engineering scaffolds, biosensors, and medical implants with enhanced functionality and biocompatibility.

6. Conclusion and Future Scope:

The discovery of polyaniline has paved the way for advancements in the field of conducting polymers and has led to numerous practical applications in various industries. It is unique among conducting polymers because it can change its conductivity in response to external stimuli like pH, temperature, or the presence of certain chemicals. This property makes it highly versatile and suitable for various applications. Over the years, researchers have made significant advancements in the synthesis and processing of polyaniline to improve its properties and expand its applications. These advancements include the development of novel synthesis methods, doping techniques, and composite materials. Despite its many advantages, polyaniline faces challenges such as poor processability, stability issues, and limited scalability in certain applications. Ongoing research aims to address these challenges and unlock the full potential of this remarkable conducting polymer.

Acknowledgment:

The authors thank to Research Centre in Electronic Science, L. V. H. College Panchavati, Nashik, India, for providing laboratory facilities.

References

1. Bhattacharya, A. and De, A., 1996. Conducting composites of polypyrrole and polyaniline a review. *Progress in Solid State Chemistry*, 24(3), pp.141-181.

2. Gospodinova, N. and Terlemezyan, L., 1998. Conducting polymers prepared by oxidative polymerization: polyaniline. *Progress in polymer science*, 23(8), pp.1443-1484.
3. Li, D., Huang, J. and Kaner, R.B., 2009. Polyaniline nanofibers: a unique polymer nanostructure for versatile applications. *Accounts of chemical research*, 42(1), pp.135-145.
4. Beygisangchin, M., Abdul Rashid, S., Shafie, S., Sadrolhosseini, A.R. and Lim, H.N., 2021. Preparations, properties, and applications of polyaniline and polyaniline thin films—A review. *Polymers*, 13(12), p.2003.
5. Zare, E.N., Makvandi, P., Ashtari, B., Rossi, F., Motahari, A. and Perale, G., 2019. Progress in conductive polyaniline-based nanocomposites for biomedical applications: a review. *Journal of Medicinal Chemistry*, 63(1), pp.1-22.
6. Zamani, F.G., Moulahoum, H., Ak, M., Demirkol, D.O. and Timur, S., 2019. Current trends in the development of conducting polymers-based biosensors. *TrAC Trends in Analytical Chemistry*, 118, pp.264-276.
7. Tran, H.D., Wang, Y., D'Arcy, J.M. and Kaner, R.B., 2008. Toward an understanding of the formation of conducting polymer nanofibers. *ACS nano*, 2(9), pp.1841-1848.
8. Zare, E.N., Motahari, A. and Sillanpää, M., 2018. Nanoadsorbents based on conducting polymer nanocomposites with main focus on polyaniline and its derivatives for removal of heavy metal ions/dyes: a review. *Environmental research*, 162, pp.173-195.
9. Dhand, C., Das, M., Datta, M. and Malhotra, B.D., 2011. Recent advances in polyaniline based biosensors. *Biosensors and Bioelectronics*, 26(6), pp.2811-2821.
10. Das, T.K. and Prusty, S., 2012. Review on conducting polymers and their applications. *Polymer-plastics technology and engineering*, 51(14), pp.1487-1500.
11. Eftekhari, A., Li, L. and Yang, Y., 2017. Polyaniline supercapacitors. *Journal of Power Sources*, 347, pp.86-107.
12. Stejskal, J., 2020. Interaction of conducting polymers, polyaniline and polypyrrole, with organic dyes: polymer morphology control, dye adsorption and photocatalytic decomposition. *Chemical Papers*, 74(1), pp.1-54.
13. Rasmussen, S.C., 2020. Conjugated and conducting organic polymers: the first 150 years. *ChemPlusChem*, 85(7), pp.1412-1429.
14. Tang, Z., Liu, S., Wang, Z., Dong, S. and Wang, E., 2000. Electrochemical synthesis of polyaniline nanoparticles. *Electrochemistry Communications*, 2(1), pp.32-35.
15. Kinyanjui, J.M., Wijeratne, N.R., Hanks, J. and Hatchett, D.W., 2006. Chemical and electrochemical synthesis of polyaniline/platinum composites. *Electrochimica Acta*, 51(14), pp.2825-2835.
16. Yang, Y. and Wan, M., 2002. Chiral nanotubes of polyaniline synthesized by a template-free method. *Journal of materials chemistry*, 12(4), pp.897-901.
17. Chao, D., Zhang, J., Li, X., Lu, X., Wang, C., Zhang, W. and Wei, Y., 2010. Synthesis of novel poly (amic acid) and polyimide with oligoaniline in the main chain and their thermal, electrochemical, and dielectric properties. *Polymer*, 51(20), pp.4518-4524.
18. Yang, C.H., Chih, Y.K., Cheng, H.E. and Chen, C.H., 2005. Nanofibers of self-doped polyaniline. *Polymer*, 46(24), pp.10688-10698.
19. Chandrasekhar, P. and Chandrasekhar, P., 2018. Introducing Conducting Polymers (CPs). *Conducting Polymers, Fundamentals and Applications: Including Carbon Nanotubes and Graphene*, pp.159-174.
20. Bhadra, S., Khastgir, D., Singha, N.K. and Lee, J.H., 2009. Progress in preparation, processing and applications of polyaniline. *Progress in polymer science*, 34(8), pp.783-810.
21. Zarrantaj, P., Ahmadi, Z., Vahabi, H., Ducos, F., Saeb, M.R. and Mozafari, M., 2018. Polyaniline in retrospect and prospect. *Materials Today: Proceedings*, 5(7), pp.15852-15860.
22. Li, D., Huang, J. and Kaner, R.B., 2009. Polyaniline nanofibers: a unique polymer nanostructure for versatile applications. *Accounts of chemical research*, 42(1), pp.135-145.
23. Tanguy, N.R., Thompson, M. and Yan, N., 2018. A review on advances in application of polyaniline for ammonia detection. *Sensors and Actuators B: Chemical*, 257, pp.1044-1064.
24. Babel, V. and Hiran, B.L., 2021. A review on polyaniline composites: Synthesis, characterization, and applications. *Polymer Composites*, 42(7), pp.3142-3157.
25. Tanguy, N.R., Thompson, M. and Yan, N., 2018. A review on advances in application of polyaniline for ammonia detection. *Sensors and Actuators B: Chemical*, 257, pp.1044-1064.