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Polyaniline and Its Nanocomposites: Synthesis, Characterization and Emerging Applications – A Review

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Abstract:
Polyaniline (PANI) is one of the most widely investigated intrinsically conducting polymers due to its environmental stability, low cost and facile synthesis. It is one of the most widely investigated intrinsically conducting polymers due to its tunable electrical conductivity (~10^{-10} to 10^2 S cm^{-1}). This review provides a comprehensive of the synthesis strategies, characterization techniques and emerging applications of polyaniline and its nanocomposites. Various synthesis methods, including chemical oxidative polymerization, electrochemical synthesis and template-assisted approaches are discussed in terms of their influence on morphology, conductivity and performance. The integration of PANI with nanomaterials such as metal oxides, carbon nanostructures and biopolymers has led to the development of nanocomposites with significantly enhanced mechanical, electrical and chemical properties. The recent advances in the application of PANI nanocomposites in gas sensing, energy storage devices, corrosion protection, environmental remediation and biomedical fields are analyzed. Emerging applications of polyaniline and its nanocomposites in fields such as gas sensing, energy storage devices (supercapacitors and batteries), corrosion protection and environmental remediation are also systematically examined. Despite notable progress, challenges related to long-term stability, processability and scalability remain. The review concludes with future perspectives aimed at addressing these limitations and exploring new opportunities for the development of high-performance PANI-based functional materials.

Keywords: Polyaniline (PANI), Conducting polymers, Nanocomposites, Chemical oxidative polymerization.

1. INTRODUCTION

In recent decades, intrinsically conducting polymers (ICPs) have emerged as a promising class of materials bridging the gap between conventional polymers and inorganic semiconductors. Among these, polyaniline (PANI) has attracted exceptional scientific and technological interest due to its unique combination of electrical conductivity, environmental stability, ease of synthesis, and low production cost [1, 2]. Unlike many other conducting polymers, PANI exhibits tunable electrical properties through simple protonic doping and dedoping processes, enabling its transition from an insulating to a highly conductive state. These advantages make PANI a versatile material for a wide range of advanced applications. Polyaniline exists in different oxidation states, namely leucoemeraldine, emeraldine, and pernigraniline, among which the emeraldine salt form is the most conductive and widely studied. The conductivity of PANI can be tailored over several orders of magnitude (from ~10^{-10} to 10^2 S cm^{-1}) by controlling synthesis conditions, dopants, and post-treatment processes [3, 4]. It exhibits good environmental stability compared to other conducting polymers, making it suitable for practical applications in diverse operating conditions. However, limitations such as poor solubility, limited mechanical strength, and reduced processability have restricted its widespread commercialization. To overcome these challenges, significant research efforts have focused on the development of PANI-based nanocomposites. The incorporation of nanomaterials such as metal oxides (e.g., ZnO, TiO_2 and SnO_2), carbon-based nanostructures (graphene, carbon nanotubes) and biopolymers into the PANI matrix has led to substantial improvements in physical, chemical, and functional properties. These nanocomposites exhibit enhanced electrical conductivity, increased surface area, improved thermal stability, and superior mechanical properties compared to pristine PANI [5-7]. The synergistic interaction between PANI and nanofillers plays a crucial role in determining the overall performance of the resulting materials.

Fig. 1 illustrates the crystal structure of polyaniline in its emeraldine salt form, highlighting the arrangement of repeating benzenoid and quinoid units along the polymer backbone. The polymer chains are organized in a layered structure stabilized by π–π stacking interactions between aromatic rings and intermolecular hydrogen bonding (N–H···anion) with dopant ions [7, 8]. The presence of counter ions (such as Cl^-) plays a crucial role in maintaining charge neutrality and enhancing electrical conductivity. The ordered packing of polymer chains within the crystal lattice facilitates efficient charge transport through polaron and bipolaron mechanisms [8, 9]. This structural organization directly influences the electrical, optical, and sensing properties of PANI, making its crystal architecture a key factor in determining overall material performance [10].

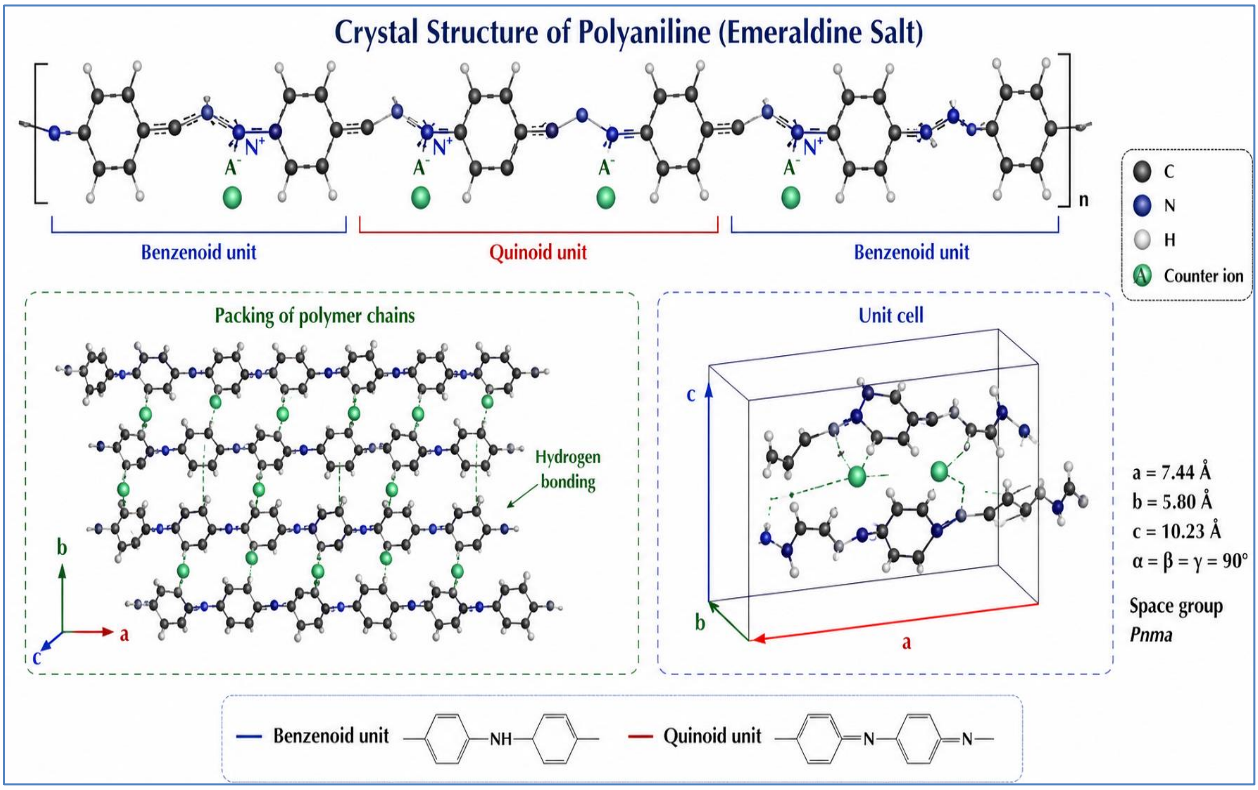


Figure 1: Polyaniline crystal structure

Polyaniline is an intrinsically conducting polymer that exhibits a unique combination of electrical, chemical, and thermal properties, making it highly suitable for advanced technological applications. As summarized in Table 1.

Table 1: Physicochemical properties of polyaniline

Property	**Typical Range / Value**	**Description / Notes**
Molecular Weight (Mw)	~10^3 – 10^5 g·mol^{-1}	Depends on synthesis method; usually polydisperse.
Electrical Conductivity	~10^{-10} – 10^2 S·cm^{-1}	Highly dependent on doping; emeraldine salt is most conductive.
Oxidation States	Leucoemeraldine, Emeraldine, Pernigraniline	Emeraldine salt is most stable and conductive.
Band Gap	~2.5 – 3.5 eV	Doping reduces band gap and increases conductivity.
Density	~1.2 – 1.4 g·cm^{-3}	Varies with morphology and doping.
Thermal Stability	Up to ~250–300 °C	Depends on dopant and structure.
Glass Transition Temperature	~80 – 120 °C	Semi-crystalline nature makes Tg less defined.
Decomposition Temperature	~300 – 500 °C	Measured via TGA.
Solubility	Insoluble in water/common solvents	Soluble in acidic media or special solvents when doped.
Morphology	Granular, nanofibers, nanotubes	Controlled by synthesis method.
Crystallinity	Amorphous to semi-crystalline	Depends on synthesis and doping.
Surface Area	~10 – 100 m^2·g^{-1}	Higher surface area improves sensing/catalysis.
Charge Transport	Polaron/Bipolaron hopping	Charge carriers formed upon doping.
Environmental Stability	Good	Stable under ambient conditions.
pH Sensitivity	High	Conductivity changes with protonation.

The synthesis of PANI and its nanocomposites can be achieved through various methods, including chemical oxidative polymerization, electrochemical polymerization, interfacial polymerization, and template-assisted techniques. Each method offers distinct advantages in controlling morphology, particle size, and structural properties [11, 12]. For instance, template-assisted synthesis enables the formation of well-defined nanostructures such as nanofibers and nanotubes, which are particularly beneficial for sensing and energy storage applications. The choice of synthesis route significantly influences the final properties and performance of PANI-based materials [12, 13].

In recent years, PANI and its nanocomposites have found extensive applications in various fields. In gas sensing, PANI-based materials demonstrate high sensitivity, fast response, and room-temperature operation [13, 14]. In energy storage, particularly in supercapacitors and batteries, PANI nanocomposites offer high specific capacitance and good cycling stability. Furthermore, their applications extend to corrosion protection, electromagnetic interference (EMI) shielding, environmental remediation (including adsorption of dyes and heavy metals), and biomedical engineering [14, 15]. The multifunctional nature of PANI makes it a key material in the development of next-generation smart devices and sustainable technologies. Despite these promising developments, several challenges remain, including long-term stability, reproducibility, scalability of synthesis methods, and degradation under harsh environmental conditions. Addressing these issues is essential for the practical implementation of PANI-based materials in industrial applications [14-16].

This review aims to provide a comprehensive overview of the synthesis, characterization, and emerging applications of polyaniline and its nanocomposites. Emphasis is placed on understanding the relationship between synthesis methods, nanostructure, and functional properties, as well as identifying current challenges and future research directions in this rapidly evolving field.

2. SYNTHESIS METHODS FOR POLYANILINE AND ITS NANOCOMPOSITES

Fig. 2 presents a comprehensive overview of the major synthesis routes used for the preparation of polyaniline (PANI) and its nanocomposites, highlighting both conventional and advanced techniques. Among these, chemical oxidative polymerization is the most widely adopted method, where aniline monomers are polymerized in an acidic medium using oxidizing agents such as ammonium persulfate (APS) or ferric chloride. This process typically occurs at low temperatures (0–5 °C) and allows control over the oxidation state, doping level, and morphology of PANI by adjusting parameters such as pH, oxidant concentration, and reaction time. In contrast, electrochemical polymerization involves the anodic oxidation of aniline on conductive substrates in an electrolyte solution, enabling the direct formation of uniform PANI thin films [16-19]. This method offers precise control over film thickness, doping level, and oxidation state, making it highly suitable for applications in sensors, supercapacitors, and electronic devices. Interfacial polymerization, carried out at the boundary of two immiscible phases (typically organic and aqueous), facilitates the formation of highly uniform PANI nanofibers with high surface area and controlled morphology, which are particularly advantageous for gas sensing and catalytic applications [19, 20].

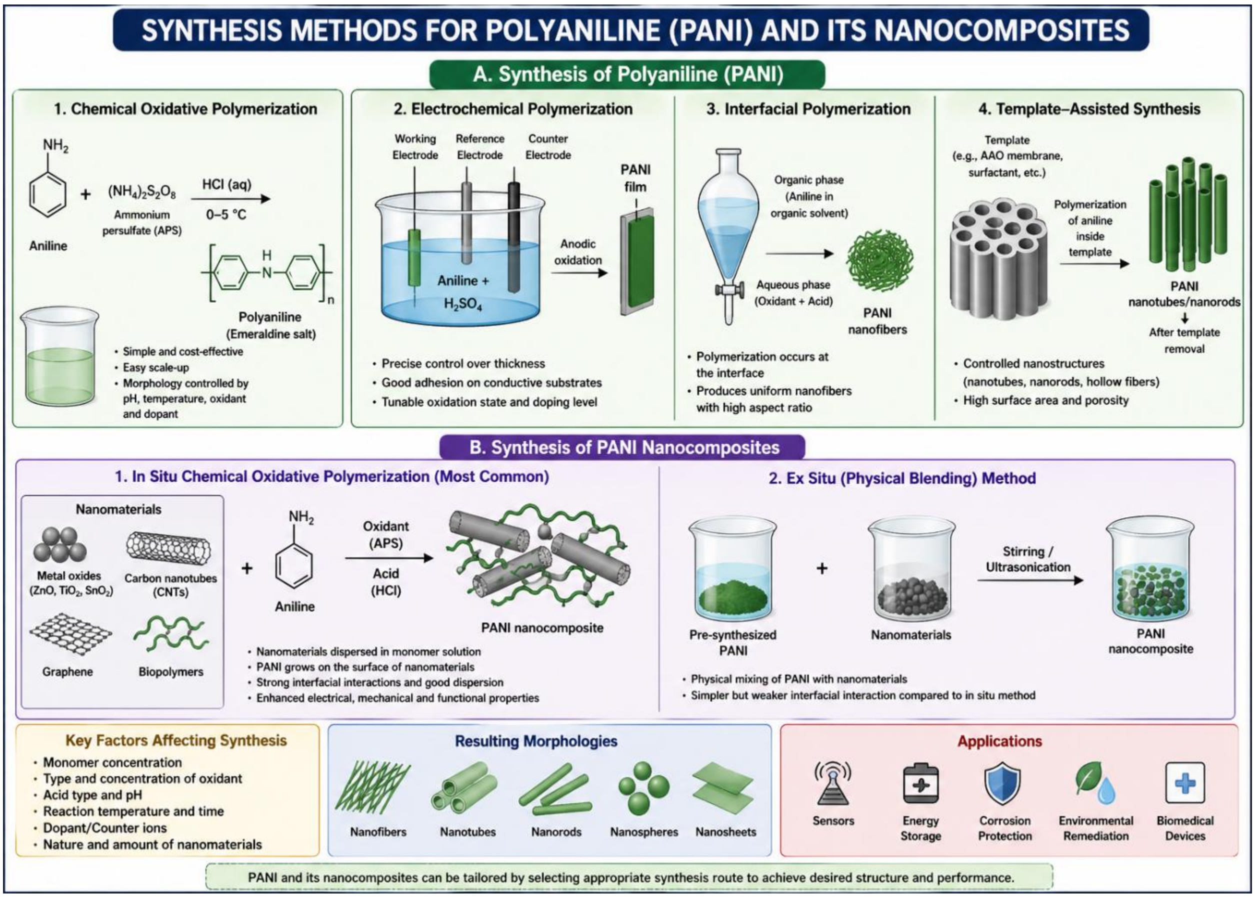
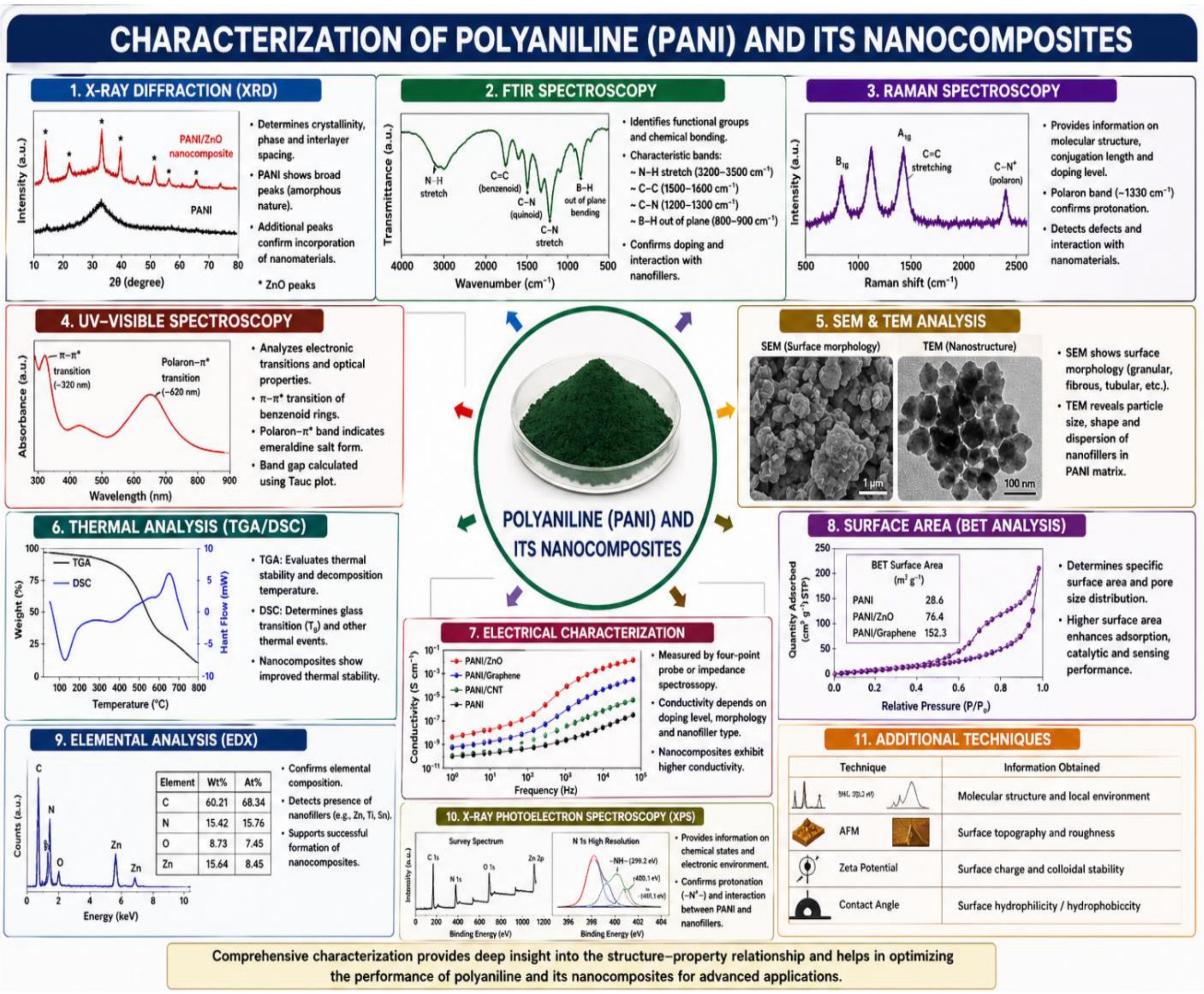


Figure 2: Synthesis methods for polyaniline and its nanocomposites

The template-assisted synthesis employs hard templates (such as anodized aluminum oxide membranes) or soft templates (such as surfactants and polymers) to guide the formation of well-defined nanostructures including nanotubes, nanorods, and nanofibers. These methods provide excellent control over size, shape, and porosity, thereby enhancing the functional performance of PANI. For the synthesis of PANI nanocomposites, two primary approaches are illustrated: in situ polymerization and ex situ (physical blending) methods. In the in situ approach, nanomaterials such as metal oxides (ZnO, TiO_2, SnO_2), carbon nanotubes (CNTs), graphene, or biopolymers are dispersed in the monomer solution, allowing PANI chains to grow directly on their surfaces, resulting in strong interfacial interactions and improved dispersion. This leads to enhanced electrical, mechanical, and chemical properties [21, 22]. On the other hand, the ex situ method involves mixing pre-synthesized PANI with nanomaterials through mechanical stirring or ultrasonication, offering simplicity but often resulting in weaker interfacial bonding.

3. CHARACTERIZATION OF POLYANILINE AND ITS NANOCOMPOSITES

Fig. 3 provides a comprehensive overview of the major characterization techniques employed to investigate the structural, morphological, chemical, optical, thermal, and electrical properties of polyaniline and its nanocomposites [18-20]. These techniques collectively enable a detailed understanding of the structure–property relationship, which is essential for optimizing the performance of PANI-based materials in applications.



CHARACTERIZATION OF POLYANILINE (PANI) AND ITS NANOCOMPOSITES

1. X-RAY DIFFRACTION (XRD)
- Determines crystallinity, phase and interlayer spacing.
- PANI shows broad peaks (amorphous nature).
- Additional peaks confirm incorporation of nanomaterials.

* ZnO peaks

2. FTIR SPECTROSCOPY
- Identifies functional groups and chemical bonding.
- Characteristic bands:
  - ~ N–H stretch (3200–3500 cm^{-1})
  - ~ C–C (1500–1600 cm^{-1})
  - ~ C–N (1200–1300 cm^{-1})
  - ~ B–H out of plane (800–900 cm^{-1})
- Confirms doping and interaction with nanofillers.

3. RAMAN SPECTROSCOPY
- Provides information on molecular structure, conjugation length and doping level.
- Polaron band (~1330 cm^{-1}) confirms protonation.
- Detects defects and interaction with nanomaterials.

4. UV–VISIBLE SPECTROSCOPY
- Analyzes electronic transitions and optical properties.
- π–π* transition of benzenoid rings.
- Polaron–π* band indicates emeraldine salt form.
- Band gap calculated using Tauc plot.

5. SEM & TEM ANALYSIS
- SEM shows surface morphology (granular, fibrous, tubular, etc.).
- TEM reveals particle size, shape and dispersion of nanofillers in PANI matrix.

POLYANILINE (PANI) AND ITS NANOCOMPOSITES

6. THERMAL ANALYSIS (TGA/DSC)
- TGA: Evaluates thermal stability and decomposition temperature.
- DSC: Determines glass transition (T_g) and other thermal events.
- Nanocomposites show improved thermal stability.

7. ELECTRICAL CHARACTERIZATION
- Measured by four-point probe or impedance spectrossopy.
- Conductivity depends on doping level, morphology and nanofiller type.
- Nanocomposites exhibit higher conductivity.

8. SURFACE AREA (BET ANALYSIS)

BET Surface Area ($m^2 g^{-1}$)	
PANI	28.6
PANI/ZnO	76.4
PANI/Graphene	152.3

- Determines specific surface area and pore size distribution.
- Higher surface area enhances adsorption, catalytic and sensing performance.

9. ELEMENTAL ANALYSIS (EDX)

Element	Wt%	At%
C	60.21	68.34
N	15.42	15.76
O	8.73	7.45
Zn	15.64	8.45

- Confirms elemental composition.
- Detects presence of nanofillers (e.g., Zn, Ti, Sn).
- Supports successful formation of nanocomposites.

10. X-RAY PHOTOELECTRON SPECTROSCOPY (XPS)
- Provides information on chemical states and electronic environment.
- Confirms protonation (–N^+–) and interaction between PANI and nanofillers.

11. ADDITIONAL TECHNIQUES

Technique	Information Obtained
NMR	Molecular structure and local environment
AFM	Surface topography and roughness
Zeta Potential	Surface charge and colloidal stability
Contact Angle	Surface hydrophilicity / hydrophobiccity

Comprehensive characterization provides deep insight into the structure–property relationship and helps in optimizing the performance of polyaniline and its nanocomposites for advanced applications.

Figure 3: Characterization for polyaniline and its nanocomposites

A combination of techniques is typically employed to evaluate different physicochemical aspects of these materials. Structural analysis using XRD reveals the amorphous to semi-crystalline nature of PANI and confirms the incorporation of nanomaterials in composite systems. Spectroscopic techniques such as Fourier transform infrared and Raman spectroscopy provide detailed information about chemical bonding, functional groups, oxidation states, and interactions between PANI and nanofillers [19-21]. Optical characterization through UV–Visible spectroscopy helps identify electronic transitions and estimate the band gap, which is closely related to conductivity and doping level. Morphological studies carried out using scanning electron microscopy (SEM) and transmission electron microscopy (TEM) reveal the surface texture, particle size, and distribution of nanostructures such as nanofibers, nanotubes, and nanosheets [21, 22]. Thermal properties are evaluated using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC), which provide insights into thermal stability and decomposition behavior. Electrical characterization techniques, including the four-point probe method and impedance spectroscopy, are used to measure conductivity and understand charge transport mechanisms [23, 24]. Surface area and porosity are determined using Brunauer–Emmett–Teller (BET) analysis, which is crucial for applications like gas sensing and catalysis. Elemental composition and chemical states are further examined using energy-dispersive X-ray spectroscopy (EDX) and X-ray photoelectron spectroscopy (XPS), confirming the presence of nanomaterials and the doping state of PANI.

4. EMERGING APPLICATIONS OF POLYANILINE AND ITS NANOCOMPOSITES

Fig. 4 highlights the wide range of emerging applications of polyaniline and its nanocomposites, driven by their unique combination of tunable electrical conductivity, environmental stability, flexibility, and ease of synthesis. One of the most significant application areas is gas sensing, where PANI-based materials exhibit high sensitivity and selectivity toward toxic and hazardous gases such as NH_3, NO_2, H_2S, and volatile organic compounds (VOCs). Their ability to operate at room temperature with fast response and recovery times makes them highly suitable for environmental monitoring, industrial safety, and healthcare diagnostics [25, 26]. The incorporation of nanomaterials such as metal oxides or carbon nanostructures further enhances sensing performance by increasing surface area and improving charge transfer mechanisms. Another important application is in energy storage devices, including supercapacitors and rechargeable batteries. PANI is widely used as an electrode material due to its high pseudocapacitance, fast redox behavior, and relatively high conductivity. When combined with nanomaterials like graphene, carbon nanotubes, or metal oxides, PANI nanocomposites exhibit improved specific capacitance, better cycling stability, and enhanced energy density [27-29]. These properties make them promising candidates for next-generation energy storage systems, particularly in portable electronics and electric vehicles [30, 31].

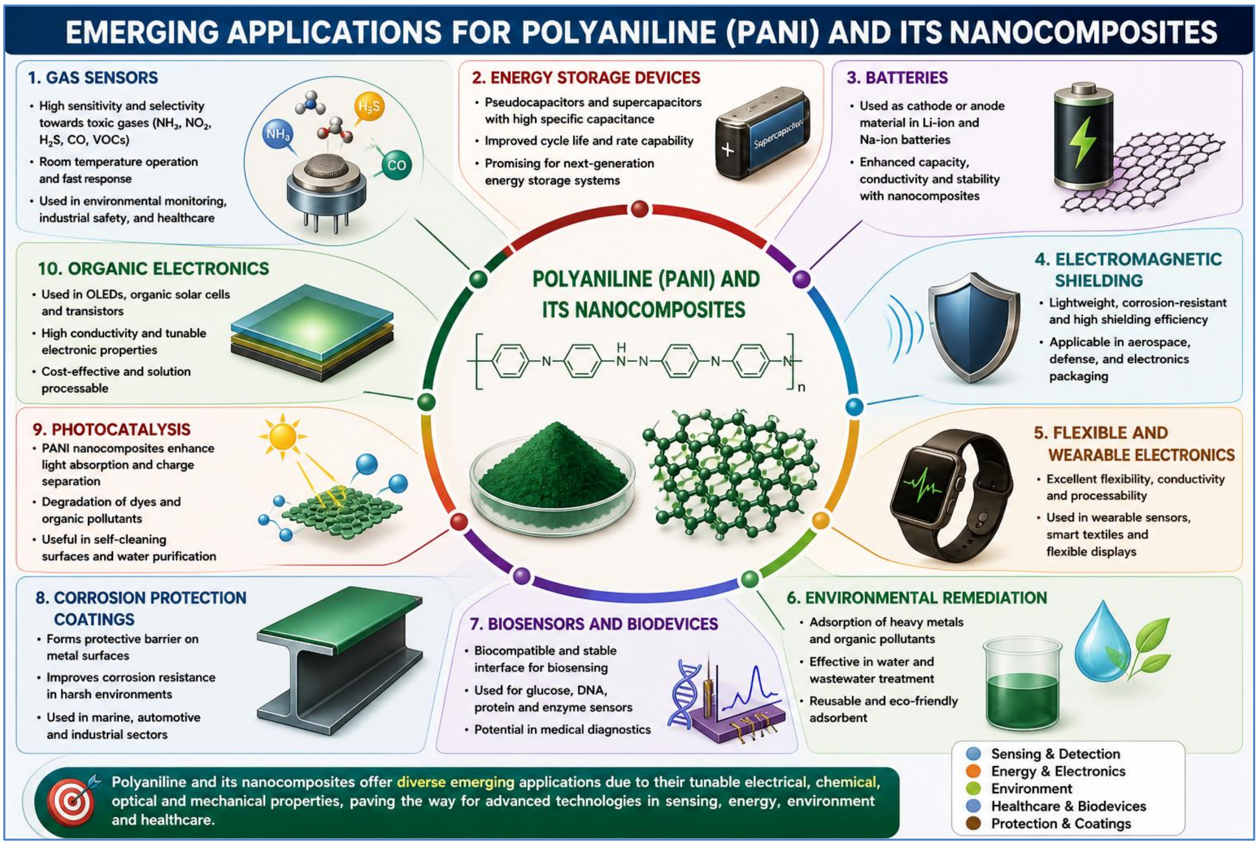


Figure 4: Emerging applications for polyaniline and its nanocomposites

In the field of electromagnetic interference (EMI) shielding, PANI-based composites are gaining attention due to their lightweight nature, corrosion resistance, and excellent shielding effectiveness. These materials are used to protect electronic devices from electromagnetic radiation and are increasingly applied in aerospace, defense, and communication technologies. PANI is extensively used in corrosion protection coatings, where it forms a protective barrier on metal surfaces and provides electrochemical protection, significantly enhancing the durability of materials in harsh environments such as marine and industrial settings [12-16]. PANI and its nanocomposites also play a crucial role in environmental remediation, particularly in water treatment applications. Due to their high surface area and adsorption capacity, they are effective in removing heavy metals, dyes, and organic pollutants from wastewater [31, 32]. Furthermore, PANI-based materials are used in photocatalysis, where they enhance light absorption and facilitate charge separation, leading to efficient degradation of pollutants under visible light [18, 19]. These properties make them highly valuable for sustainable and eco-friendly environmental technologies. In the biomedical field, PANI exhibits excellent potential for biosensors and biodevices due to its biocompatibility, electrical conductivity, and ability to facilitate electron transfer [19, 20]. It is used in the detection of biomolecules such as glucose, DNA, proteins, and enzymes, and has promising applications in medical diagnostics and healthcare monitoring. Moreover, the development of flexible and wearable electronics has further expanded the scope of PANI, as its mechanical flexibility and conductivity make it suitable for smart textiles, flexible sensors and electronic skin [30-32].

5. LITERATURE SURVEY

Extensive research has been carried out on polyaniline and its nanocomposites due to their versatile physicochemical properties and wide-ranging applications. Early foundational work by Alan J. Heeger et al. (1988) highlighted the significance of conducting polymers, establishing PANI as a promising material for electronic applications [33]. A. G. MacDiarmid et al. (1991) demonstrated the tunable conductivity of PANI through protonic doping, which significantly advanced its application potential [34]. Later, W. S. Huang et al. (1986) investigated the chemical synthesis of PANI via oxidative polymerization, providing a basis for scalable production methods. Further studies focused on improving the structural and functional properties of PANI through nanocomposite formation [35]. S. Bhadra et al. (2009) reviewed the synthesis, properties, and applications of PANI, emphasizing its role in advanced materials [36]. N. Gospodinova et al. (1998) explored the influence of synthesis conditions on the morphology and conductivity of PANI, showing that nanostructuring significantly enhances performance [37]. Research by M. Gerard et al. (2002) demonstrated the application of PANI in gas sensing, highlighting its sensitivity to gases such as ammonia and nitrogen dioxide [38]. In the field of nanocomposites, J. Stejskal et al. (2010) reported that incorporating metal oxides and carbon nanomaterials into PANI improves its electrical conductivity, thermal stability and surface area [39]. Studies by K. R. Prasad et al. (2011) showed that PANI-based nanocomposites exhibit enhanced electrochemical performance, making them suitable for supercapacitor applications [40]. Furthermore, X. Zhang et al. (2013) investigated PANI/graphene composites and reported significant improvements in charge transport and cycling stability. Recent research trends focus on multifunctional applications of PANI nanocomposites [41]. Y. Wang et al. (2018) explored PANI-based materials for environmental remediation, demonstrating high adsorption capacity for heavy metals and dyes [42]. L. Liu et al. (2020) reported the use of PANI nanocomposites in flexible and wearable electronics due to their excellent mechanical flexibility and conductivity [43]. R. Kumar et al. (2022) highlighted the role of PANI in biomedical applications, particularly in biosensors and drug delivery systems [44]. Fu et al. (2023) reported that PANI–TiO_2 heterostructures exhibit improved photocatalytic efficiency due to enhanced visible light absorption and reduced charge recombination, making them suitable for environmental remediation applications [45]. Bera et al. (2024) investigated PANI-based composites for electromagnetic interference (EMI) shielding and found that these materials exhibit excellent dielectric and microwave absorption properties, indicating their potential in advanced electronic and defense applications [46]. Further, Yadav et al. (2024) highlighted that continuous developments in doping strategies, particularly with chalcogen elements such as selenium and tellurium, significantly enhance the electrical and optical properties of PANI nanocomposites, opening new avenues for optoelectronic applications [47]. Meena et al. (2024) demonstrated that PANI-based nanocomposites act as efficient heterogeneous catalysts for the reduction of hazardous water pollutants, emphasizing their role in sustainable environmental technologies [48]. In addition, Gutnik et al. (2024) reported that PANI combined with carbon nanomaterials exhibits superior performance in energy storage devices, sensors, and anticorrosive coatings due to improved conductivity and surface area [49]. Moreover, recent comprehensive reviews by researchers such as Zhang et al. (2024) have emphasized that various synthesis techniques, including chemical oxidative polymerization, electrochemical polymerization, and vapor phase methods, play a crucial role in tailoring the morphology and functional properties of PANI nanocomposites [50]. Another study in 2023 on PANI–epoxy nanocomposites demonstrated that advanced characterization techniques such as XRD, SEM, and TEM are essential for understanding morphology and crystallinity, which directly influence thermal and dielectric properties [51]. The literature indicates that continuous advancements in synthesis techniques and nanocomposite development have significantly enhanced the performance of PANI-based materials. The integration of nanotechnology with conducting polymers has opened new avenues for applications in sensing, energy storage, environmental protection and biomedical engineering, making PANI a key material in modern materials science research.

CONCLUSIONS

In conclusion, polyaniline and its nanocomposites have emerged as highly versatile and promising materials due to their unique combination of tunable electrical conductivity, environmental stability, cost-effectiveness, and ease of synthesis. This review has comprehensively discussed various synthesis methods, including chemical oxidative polymerization, electrochemical techniques, and advanced approaches such as interfacial and template-assisted methods, which enable precise control over morphology and functional properties. Detailed characterization using techniques such as XRD, FTIR, SEM/TEM, UV–Vis, and thermal analysis has been shown to be essential for understanding the structure–property relationships that govern the performance of PANI-based materials. The incorporation of nanomaterials such as metal oxides, carbon nanostructures, and biopolymers into the PANI matrix significantly enhances its physicochemical properties, leading to improved conductivity, thermal stability, surface area, and mechanical strength. As a result, PANI nanocomposites have demonstrated remarkable potential in a wide range of emerging applications, including gas sensing, energy storage, electromagnetic interference shielding, corrosion protection, environmental remediation, and biomedical devices. Despite these advancements, challenges such as limited processability, long-term stability, and large-scale fabrication remain critical barriers to commercialization. Future research should focus on developing novel synthesis strategies, improving material stability, and exploring sustainable and scalable production techniques. The deeper insights into interfacial interactions and charge transport mechanisms will further enhance the performance of PANI-based systems. The continued integration of nanotechnology with conducting polymers is expected to unlock new opportunities, positioning polyaniline and its nanocomposites as key materials for next-generation advanced technologies.

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