Journal of
Composites Science

Review

Anthranilic Acid: A Versatile Monomer for the Design of Functional Conducting Polymer Composites

Rachel McCormick [1], Emily Buckley [1], Paul J. Donnelly [1], Victoria Gilpin [1], Regan McMath [1], Robert B. Smith [2], Pagona Papakonstantinou [1] and James Davis [1,*]

[1] School of Engineering, Ulster University, Belfast BT5 1ED, UK
[2] Institute for Materials and Investigative Sciences, School of Engineering and Computing, University of Central Lancashire, Preston PR1 2HE, UK; rbsmith@uclan.ac.uk
* Correspondence: james.davis@ulster.ac.uk

Abstract: Polyaniline has been utilized in various applications, yet its widespread adoption has often been impeded by challenges. Composite systems have been proposed as a means of mitigating some of these limitations, and anthranilic acid (2-aminobenzoic acid) has emerged as a possible moderator for use in co-polymer systems. It offers improved solubility and retention of electroactivity in neutral and alkaline media, and, significantly, it can also bestow chemical functionality through its carboxylic acid substituent, which can greatly ease post-polymer modification. The benefits of using anthranilic acid (as a homopolymer or copolymer) have been demonstrated in applications including corrosion protection, memory devices, photovoltaics, and biosensors. Moreover, this polymer has been used as a versatile framework for the sequestration of metal ions for water treatment, and, critically, these same mechanisms serve as a facile route for the production of catalytic metallic nanoparticles. However, the widespread adoption of polyanthranilic acid has been limited, and the aim of the present narrative review is to revisit the early promise of anthranilic acid and assess its potential future use within modern smart materials. A critical evaluation of its properties is presented, and its versatility as both a monomer and a polymer across a spectrum of applications is highlighted.

Keywords: anthranilic acid; polyaniline; polyanthranilic acid; conducting polymer; electrode

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Citation: McCormick, R.; Buckley, E.; Donnelly, P.J.; Gilpin, V.; McMath, R.; Smith, R.B.; Papakonstantinou, P.; Davis, J. Anthranilic Acid: A Versatile Monomer for the Design of Functional Conducting Polymer Composites. *J. Compos. Sci.* **2024**, *8*, 208. https://doi.org/10.3390/jcs8060208

Academic Editors: Xiaofeng Lu and Shanju Zhang

Received: 24 April 2024
Revised: 21 May 2024
Accepted: 31 May 2024
Published: 3 June 2024

1. Introduction

Research into intrinsically conducting polymers (ICPs), first established by the pioneering work of Shirakawa, MacDiarmid, and Heeger in 1977 [1], has intensified in recent times, with polyacetylene being eclipsed by a spectrum of new conjugated systems [2–7]. Polypyrrole, polythiophene, polyaniline, and their associated derivatives are the more common of the new variants and are among the few that are stable enough, under normal processing conditions, to be considered for use in a wide range of applications ranging from energy generation and storage to environmental remediation [2–7]. There has been a tremendous increase in the production and characterization of these polymers, leading to an extensive library of systems with unique electrical and optical properties. Ironically, polyaniline (PANI) is far from a new discovery, and its preparation was reported in the 1800s by various groups [8]. It is only in modern times that the true potential of the original aniline black has been recognized, and it is increasingly being proposed to be a key component in the design of smart devices. The applications in which it has been applied have included electromagnetic shielding, photothermal therapies, photovoltaic generation and catalysis, energy storage, membrane separation, molecular electronics and memory devices, chemical and biosensing, anti-corrosion coatings, organic light-emitting diodes, and electrorheological materials [9–17]. The use of PANI has also taken many physical forms, ranging from films to fibers and nanoparticles, and found extensive use in the formation of composite materials [10–12]. The relative significance of PANI systems within the conducting polymer research base is highlighted in Figure 1, where the numbers of peer-reviewed publications citing the common conducting polymers are compared.

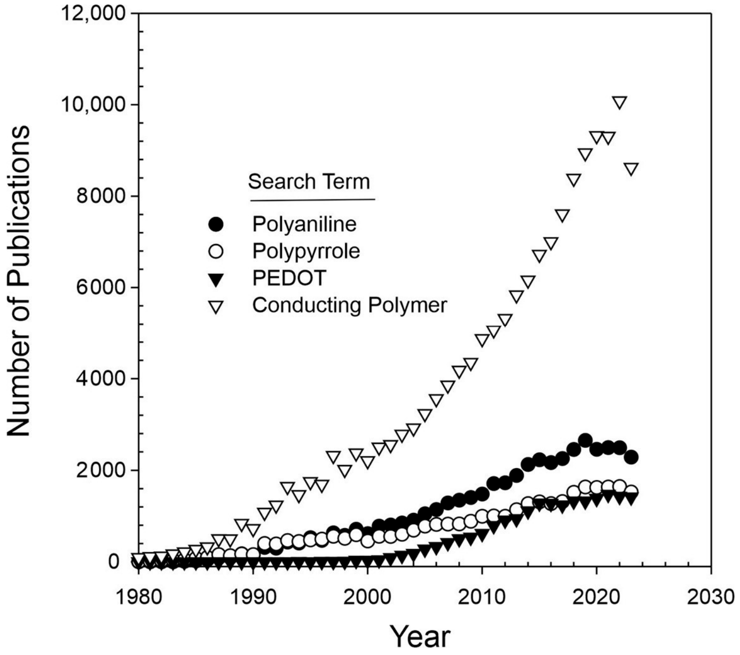

Figure 1. Trends in peer-reviewed publications reporting the use of conducting polymers. Figures are based on ISI Web of Science data.

The ease with which PANI can be prepared through both chemical and electrochemical oxidation and its low cost, stability, conductivity upon doping, and unique protonic doping process have proven to be attractive within the bioelectronics sector [17]. Despite these formidable merits, it nevertheless suffers from considerable practical limitations. In its powdered form, its processability is very limited in that it is quite an intractable material, being insoluble in common organic solvents. Moreover, it is not amenable to melt processing and degrades at high temperatures [13,18]. Its conductivity is also limited to highly acidic solutions, with a loss of electrochemical activity observed in solutions with a pH greater than 4 [19,20]. The core backbone of PANI is also relatively chemically inert, which can be problematic when attempting to tailor the interface to specific applications. As such, there have been significant efforts made to find alternatives that can address the limitations associated with PANI. Co-polymerization with aniline derivatives possessing acidic functional groups (sulphonic [21,22], phosphonic [23], and carboxylic acids [19,24–35]) has been proposed as a means of mitigating the processing and conductivity factors whilst also creating opportunities for improved chemical functionality. The latter could allow postproduction modification, which is an increasingly significant prerequisite for biosensing applications. In particular, anthranilic acid, or 2-aminobenzoic acid, has emerged as a low-cost yet highly versatile monomer for use in the preparation of copolymer PANI systems (Figure 2), wherein the carboxylic acid substituent can address many of the core limitations of PANI homopolymers.

It has been previously reported that the presence of acidic groups within a chain can modify the microenvironment of a polymer network—shifting the local pH and allowing the retention of conductivity, where the pH > 4 [19,24,25]. Moreover, the presence of the polar carboxylic groups enhances solubility [25,26] and processability, and it also provides the chemical flexibility for further modification that allows such systems to be tuned to a particular application. These features have led to the use of anthranilic acid as a modifying agent in a wide range of copolymer systems beyond PANI.

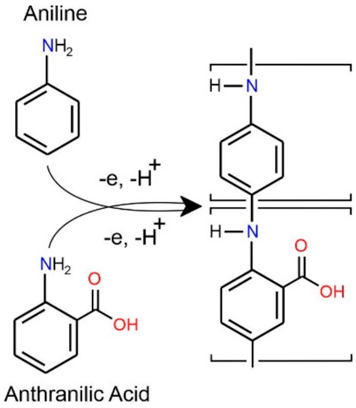

Figure 2. Typical head-to-tail co-polymerization of aniline and anthranilic acid.

Some of the more common applications in which anthranilic acid in the form of a homopolymer, copolymer, or composite have been characterized [36–81] are highlighted in Table 1.

Table 1. Range of applications for polymers incorporating anthranilic acid.

Polymer Composition	Application	Refs
PANI-PAA	Absorbents	[36]
PANI-PAA, CS	Anode Protection	[37,38]
PEG-PAA, PAA, PANI-PAA	Anti-corrosion	[39–41]
PAA	Catalysis	[42–44]
PANI-PAA	Magnetic Materials	[45–50]
PANI-PAA, PAA	Memory Storage	[51–53]
PANI-PAA, PAA	Nanomaterials	[42–50,54–64]
PAA-PDA	Photovoltaics	[49,50,55,58]
PAA, PANI-PAA, PAA-PP	Sensors	[61,65–80]
PANI-PAA	Waste Water Treatment	[59,81]

PANI = Polyaniline, PAA = Polyanthranilic Acid, PDA = Phenylene Diamine; PEG = Polyethylene glycol; CS = Chitosan; PP = Polypyrrole.

While there is an extensive body of reviews dedicated to PANI and its various applications [10–17], information on anthranilic acid and its application as a conductive polymer/composite has yet to be collated. The anthranilic acid unit offers a number of distinct features that can dramatically enhance the properties of conventional conducting polymers such as a polyaniline. These include greater solubility, self-doping/retention of activity at higher pH levels, and providing a versatile functional group that can interact with metal ions, yielding metal nanomaterials. As interest in biosensing grows, the carboxylate group can also be invaluable as a means of tethering biological agents. There are no reviews on the polymer properties of anthranilic acid, and hence the aim of the present report, therefore, has been to train a spotlight on the diversity of roles that anthranilic-acid-based polymers (either as homopolymers or copolymers with respect to PANI) can fulfil such that its functional capabilities can be highlighted and exploited in the design of new smart materials and devices.

2. Origins and Chemical Significance

Anthranilic acid is a key metabolite in a number of biochemical pathways [82–85] and has also been exploited in numerous therapeutic applications. In many cases, these have helped to inform the subsequent translation of this molecule to engineering contexts—whether for advanced materials or sensor applications. While reviews of anthranilic chemistry are available [86–88], the more pertinent contextual points that can have a direct impact on its adoption and its ultimate application are summarized here.

Anthranilic acid was originally thought to be a necessary dietary factor and originally denoted as Vitamin L1 [82]. It has since been found to be non-essential for human health, but, nevertheless, it remains a key intermediate in human biochemistry. It has been implicated as both a diagnostic and prognostic marker for conditions including chronic brain injury, Huntington's disease, stroke, depression, coronary heart disease, intrathoracic disease, and osteoporosis [82–85]. Anthranilic acid arises through the catabolism of tryptophan via the Kynurenine pathway and is normally a momentary intermediate that undergoes further conversion (summarized in Figure 3), eventually resulting in the production of nicotinamide (NAD+).

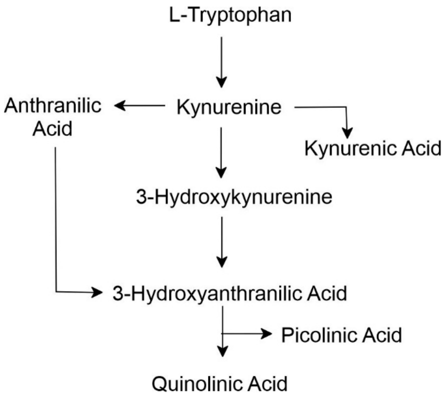

Figure 3. Kynurenine pathway leading to the production of anthranilic acid (adapted from [82]).

The in vivo conversion of anthranilic acid is enzymatic and otherwise chemically stable such that dysregulation of the kynurenine pathway can lead to its accumulation. Another key source of anthranilic acid is the gut microbiome, where microbes within the gastrointestinal tract share similar Kynurenine enzymatic machinery to the mammalian host [83,84]. It is noteworthy that there is considerable clinical interest in monitoring changes in systemic anthranilic acid concentrations, but it could also be a critical fecal marker for gut health.

Anthranilic acid has long been established as a versatile precursor in organic synthesis and forms the core of many bioactive compounds. There is an extensive body of literature on its use for the preparation of anticancer, antimicrobial, insecticidal, anti-inflammatory, and antiviral drugs offering a spectrum of therapeutic uses [86–88]. The amine and carboxylic acid functionalities within this molecule serve as sites through which its structure can be modified to target particular biological pathways, with the aim of inducing some therapeutic action. These same properties are key to the versatility of polymers incorporating anthranilic acid monomer units where the carboxylate substituents are harnessed to tailor the functionality of the polymer backbone.

3. PANI—Anthranilic Acid Polymerization

3.1. Polymerization Mechanism

The polymerization of aniline or its derivatives (including anthranilic acid) is well documented and initiated by the oxidation of the aromatic amino functionality, leading to the production of a radical cation [89,90]. The generic reaction scheme is shown in Figure 4, where the R group can be either H (for aniline) or COOH (for anthranilic acid). Upon the generation of the radical cation (II), the unpaired electron can be delocalized within the aromatic ring with resonance forms favoring the ortho (III) and para (IV) positions.

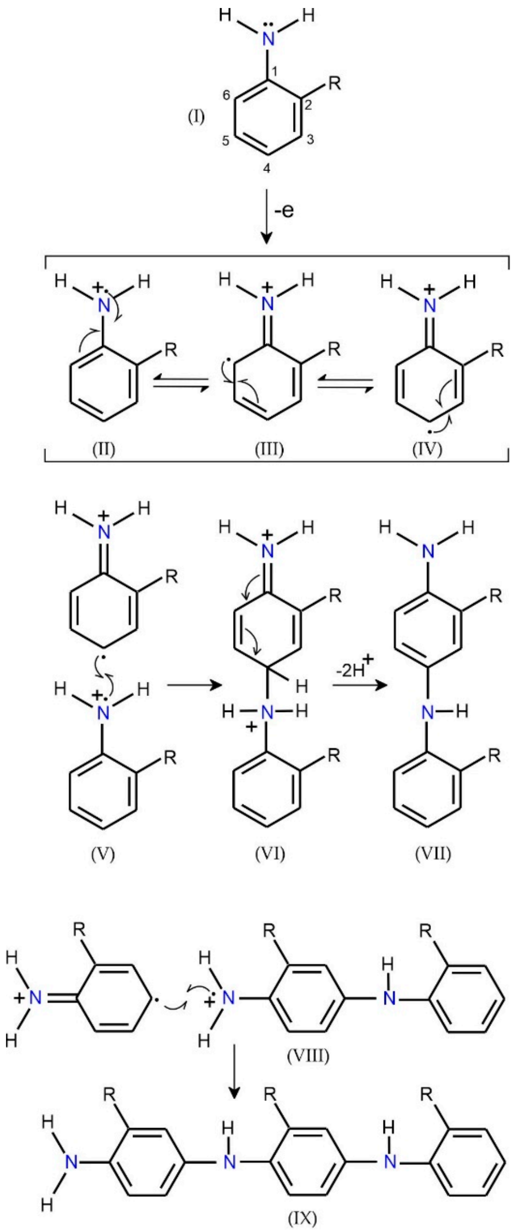

Figure 4. Oxidative polymerization pathway for aniline derivatives highlighting head-to-tail coupling through the 4 position, where R = H (for aniline) or R = COOH (for anthranilic acid).

In general, PANI (or those derivatives with a substituent in the 2 position) will typically form long linear chains through head-to-tail coupling (via the para position), as highlighted in structures (V→VII). The subsequent oxidation of the amino "head" of the resulting dimer (VIII) continues the propagation of the chain (VIII→IX) and is repeated to yield the long linear chain associated with PANI. The fact that the carboxylate group (COOH) on anthranilic acid is in the ortho position also facilitates head-to-tail coupling and minimizes steric issues that would normally shorten chain length. However, the latter can be affected by the general reactivity of the monomer. It has been reported that PANI is some 7000 times more reactive than anthranilic acid due to the lower nucleophilicity of the amino functional group on the latter [24–27]. This can significantly impact the outcome of mixed-monomer polymerization, where the anthranilic content within the final polymer has been found to be much lower than the original ratio used in the monomer solution. It is only when the anthranilic acid monomer is the major component that the final polymer becomes enriched with the former [25,27].

All three aminobenzoic acid isomers (with the COOH group being positioned either ortho, meta, or para with respect to the amino group) have been used as copolymers in PANI systems [74,91,92]. In the case of the 4-aminobenzoic acid (4ABA) isomer, the COOH group blocks the 4-position, thereby impeding head-to-tail coupling, and would be expected to force ortho coupling, which would lead to a much more sterically complex polymer structure, as indicated in Figure 5.

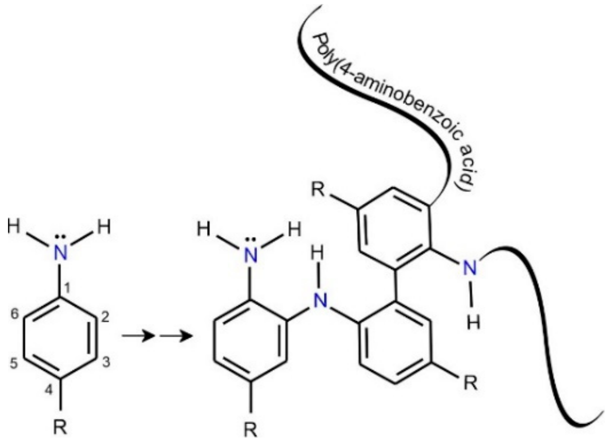

Figure 5. Steric restriction forcing oxidative polymerization to progress through the 2-position (ortho).

Sarvani et al. (2016) employed 4-aminobenzoic acid not as a homopolymer but rather as an electropolymerizable end cap, which was added to a hyperbranched aliphatic polyester. Here, the 4ABA was the terminating unit at the end of each branch, which could then be oxidized in the presence of aniline to crosslink the polymer chains for use as cellular scaffolds [92]. While the 4ABA derivative leads to the ortho-coupled polymer structure (Figure 5), in principle, it could be envisaged that polymerization of the ortho and meta substituted derivatives would result in chains with near identical chemical structures, as indicated in Figure 6. In both cases, the amino and carboxylate functionalities end up being adjacent (1,2 relative positioning) to each other as a consequence of the head-to-tail coupling process. Although the end chains may be structurally similar, steric issues will undoubtedly arise in the initial polymerization process, wherein the meta substituted COOH could impede subsequent head-to-tail coupling. Benyoucef et al. (2005) found that the meta derivative was more difficult to oxidize than the ortho and was associated with a greater degree of chain branching and shorter chains [24]. The structural consequences of ortho and meta anthranilic acid, however, have yet to be fully clarified [74,91].

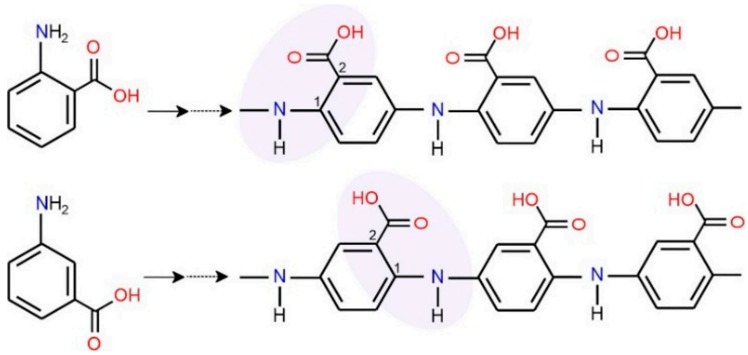

Figure 6. Despite differences in the initial position of the COOH group in the aniline derivative, the end polymer chains are structurally indistinguishable.

3.2. Chemical Polymerization

The formation of this polymer occurs readily through the oxidation of the amino group and can be achieved using either chemical or electrochemical means [89,90]. The electron-withdrawing nature of the COOH substituent renders the anthranilic acid derivative less active than aniline, and it has been reported that the preparation of a PAA homopolymer results in a lower yield when compared with PANI under the same conditions [24–27]. The most common chemical route for the preparation of PANI, PAA, or PANI-PAA copolymers is through oxidation with ammonium persulphate ($S_2O_8{}^{2-}$, APS) in an acidic solution, typically resulting in significant quantities of the respective polymer. In some cases, the APS is supplemented with a redox initiator such as ferrous sulfate ($FeSO_4$) to enhance the polymerization rate [92,93]. The Fe^{2+} ions have a lower oxidation potential than the anthranilic acid and react with the APS to produce sulfate radical anions in accordance with Equation (1).

$$S_2O_8{}^{2-} + Fe^{2+} \rightarrow SO_4{}^{2-} + SO_4{}^{-} + Fe^{3+} \tag{1}$$

Polymerization conducted in the presence of Fe^{2+} has been shown to proceed at a much greater rate than that conducted in the absence of a mediator, where it has been proposed that the main oxidative protagonist is the sulphate radical anion rather than APS itself [23]. While APS is the most common agent used for the polymerization of anthranilic acid and supporting monomers, metal ion oxidants such as Fe(III) [36,42,46], Cr(VI) [26,44,49,56,58,81], Pd(IV) [42], and Au(III) [61,63,74,76] have also been used to form polymeric structures—usually when the development of nanostructures is required, and these are discussed in more detail in Section 4.1.

3.3. Electrochemical Polymerization

The intractable nature of the PANI product arising from chemical polymerization can create obvious issues regarding the subsequent processing of the material—especially when considering the placement of the polymer within microdevice architectures. Electropolymerization addresses many of these issues, offering a greater degree of control over the spatial deposition of a polymer as well as its thickness. It also enables a uniform distribution of the film across nonplanar substrates such as wires or mesh geometries. It must be noted that the presence of the electron-withdrawing COOH on anthranilic acid will increase the oxidation potential of the monomer [20,24]. This is of particular importance when considering co-polymerization with more easily oxidizable monomers such as pyrrole [70].

3.4. Polymer Doping and pH Dependence

MacDiarmid proposed three idealized types of PANI: leucoemeraldine (fully reduced), emeraldine (half-oxidized), and pernigraniline (fully oxidized) [94]. Among these, the emeraldine form is the most stable and conductive—with the latter being achieved through doping with a protonic acid. Hence, most of the polymerization processes are conducted in the presence of a suitable acid (typically HCl, or H_2SO_4). While anthranilic acid exhibits these same states, it must be noted that its carboxylate group, in contrast to the case for PANI, enables self-doping [20,24–29]. The main transitions between the various states in a PAA homopolymer are detailed in Figure 7.

A high degree of protonation at the imine nitrogen atoms within the emeraldine form (Figure 7C) is needed to maintain conductivity, and, as such, PANI is known to lose activity above pH 4 [25–29]. Modification with acid functionalities (sulphonic, phosphonic, and carboxylic) has been extensively investigated as a means of self-doping that can broaden the electrochemically active pH range, but both the sulphonic and phosphonic systems are procedurally complex [21–23]. Monomers with sulphonic acid substituents are difficult to directly polymerize, thereby requiring post-modification processing with fuming sulfuric acid [22]. While these approaches have successfully yielded conductive films with activity beyond pH 4, the harsh post-polymer conditions required to achieve functionalized films could be prohibitive for some applications. It is also important to note that with regard to PANI, the redox transitions necessitate the transport of anions in and out of the film to maintain charge balance. In the case of the self-doped systems (Figure 7), the film is anion-independent, wherein the acid groups directly compensate for the charge generated along the polymer backbone [24]. As such, anions are not exchanged with the film; rather, excess positive charge is eliminated by the expulsion of protons.

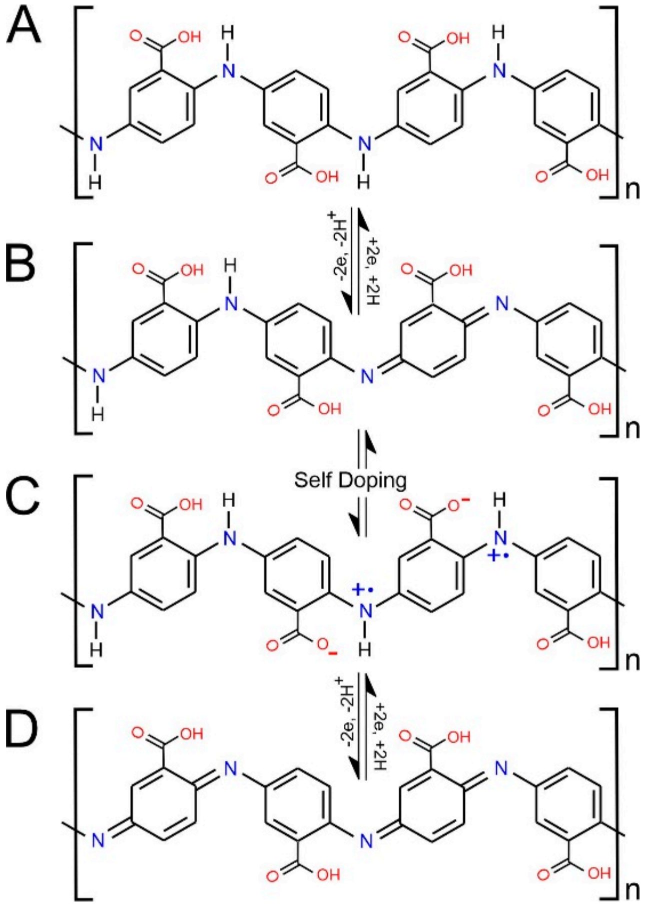

Figure 7. (**A**) Leucoemeraldine; (**B**,**C**) emeraldine base and salt; (**D**) pernigraniline. (Adapted from [31].)

3.5. Polymer Solubility and Processing

In general, the emeraldine base (EB) of PANI is typically obtained as a dark powder and is insoluble in most solvents. This intractable nature is attributed to its rigid polymer backbone and the H bond interactions between neighboring chains. It is also noteworthy that the EB form is also unstable with respect to melt processing, which further hampers its commercial/industrial application. In contrast, the COOH group of the anthranilic acid monomer unit within PANI-PAA copolymers increases the inter-chain spacing as a consequence of steric considerations, which can subsequently weaken H bonding and increase solubility [17,18]. An example of a situation where enhanced solubility can lead to the formation of hitherto unobtainable PANI composites is provided in the work by Gupta et al. (2011). Here, the solubility of PAA in tetrahydrofuran facilitates its direct mixing with a carboxylated PVC to yield a solid-state membrane for use in pH sensing [95].

4. Polyanthranilic Acid Applications

It is clear that anthranilic acid, when copolymerized with aniline, can yield polymers with better processing capability and retention of conductivity in environments with higher pH levels. The applicability of anthranilic acid along with a critical appraisal of its value are discussed in turn within the following sections.

4.1. Nanomaterials/Nanocomposites

Polymers and copolymers of anthranilic acid have been used to yield a 3D matrix within which nanoparticles can be incorporated. In such cases, a PAA or PANI-PAA hybrid can be utilized as a means of selectively embedding the core ion, which is subsequently converted to the corresponding oxide—usually through thermal treatment [18,55–58]. This has been performed for a number of metal oxides and is described in detail in Section 4.2. The chemical polymerization of PAA or its copolymers can, however, also be manipulated to yield polymer composite structures that possess nano dimensions. The latter typically include nanoparticles, nanorods, and nanofibers. While electropolymerization inevitably leads to the deposition of films on the electrode substrate, chemical polymerization offers more opportunities to significantly alter morphological character through the simple manipulation of the reaction medium. This was demonstrated by Khalil et al. (2013), who showed that the polymer's shape could be transformed from spherical to fiber-like by changing the polymerization conditions [96]; the results of this research are summarized in Figure 8.

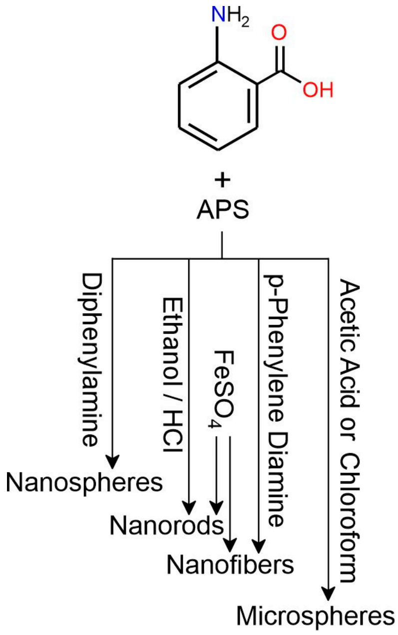

Figure 8. Effect of reaction conditions on the morphology of the polymers resulting from the chemical polymerization of anthranilic acid with ammonium persulphate (APS). (Adapted from [96].)

A number of core–shell strategies have also arisen and typically involve the polymerization of anthranilic acid in the presence of a metal nanoparticle. This can involve coating the outside of an existing metal nanoparticle or system, wherein the oxidant that induces the polymerization then becomes the core. In terms of coating pre-existing nanoparticles, TiO_2 [44] and magnetite Fe_3O_4 [45–49] are the more common applications that involve photocatalysis, photovoltaics, energy, and remediation. Chao et al. (2006) exploited the O,N coordination capabilities of the iron oxide to attach monomeric anthranilic acid [45]. The resulting anthranilic-acid-capped Fe_3O_4 was precipitated and then placed in an aniline solution along with the oxidant to produce well-dispersed Fe_3O_4-PAA-PANI nanoparticles.

However, employing metal ion oxidants such as Pt, Pd, and Au allows a more customized approach, potentially simplifying procedural methods. In this case, oxidation of the aniline/anthranilic acid monomer leads to the simultaneous reduction of the metal ion, which then serves as the nanoparticle core. This strategy has been used for PAA [42,63] and various copolymer mixtures. Mallick et al. (2008) employed palladium acetate in the presence of anthranilic acid to simultaneously oxidize the latter to PAA whilst reducing Pd(IV) to a metal. This led to the formation of 2 nm Pd nanoparticles dispersed within the PAA matrix and was subsequently used as a catalyst for ethylene hydrogenation [42]. Similarly, Golshaei and colleagues (2017) exploited the oxidizing capabilities of Au(III) with m-anthranilic acid to yield discrete PAA-Au core–shell structures [65].

4.2. Metal Ion Complexation

Anthranilic acid's metal chelation capabilities are well established, and it has found widespread application as a versatile ligand. Ros et al. (2002) demonstrated that the chemical modification of carbon fibers with anthranilic acid through chemical attachment rather than polymerization led to the creation of a functional surface that could coordinate rhodium ions [43]. Carboxylate groups on the fiber were activated via an acid chloride reaction pathway (in contrast to the carbodiimide approach discussed later) that coupled them to the amino group of the anthranilic acid, yielding an amide. Coordination of the rhodium was achieved through the free carboxylate of the tethered anthranilic acid and the amide nitrogen. The subsequent reduction of the coordinated Rh ions generated nanoparticle clusters of the metal, which were shown to be catalytically active [43]. One issue with such an approach is that surface coverage is essentially limited to a monolayer, which will inevitably reduce the yield of material.

Rather than employing anthranilic acid as an individual ligand, polymerization can transform the metal-binding capacity from being geared toward a 2D surface to a 3D matrix, which is dependent upon the thickness of the film. The formation of PAA (as noted in Figure 7) will still retain the metal complexing components (amine and carboxylate) yet can be easily grown and thereby find similar applications in sensing, catalysis, and remediation. Hosny et al. (2016) demonstrated the capability of copolymers of anthranilic acid and 2-aminophenol to engage in the complexation of Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, and Fe^{3+} ions [50,55]. In particular, Hosny and coworkers exploited various anthranilic acid composites as a means of coordinating metal ions that would then act as the seed for the production of oxide nanoparticles [55–57]. It was anticipated that the three-dimensional matrix presented by the polymer could aid in preventing aggregation, thereby leading to spatially distinct clusters. Thermal decomposition of the PAA-POAP-Fe(III) was found to yield α-Fe_2O_3 nanoparticles with an average size of 34 nm [55,56]. A similar templating approach was demonstrated by Hossainy et al. (2018) for the production of CuO through the thermal decomposition of coordinated Cu [60]. While thermal treatment (800 °C) can yield the respective metal oxide nanoparticle, Ogura et al. (1999) have shown that the application of heat, at a considerably lower temperature, i.e., 280 °C, has a direct effect on the polymer backbone itself, provoking the loss of the carboxylate group and effectively resulting in the formation of PANI [18].

In contrast to using anthranilic polymers as a means of generating nanoparticles, Mahmoud et al. (2020) used a variant of PAA as a matrix for incorporating carbon quantum dots (CQDs) for use as a fluorescent nano-absorbent [59]. Rather than the simple head-to-tail oxidative polymerization highlighted in Figure 4, Mahmoud and colleagues employed a single-step condensation reaction involving carbon quantum dots in the presence of anthranilic acid, formaldehyde, and phthalic acid to produce the methylene-linked polymer highlighted in Figure 9.

In this system, uranyl (VI) ions from wastewater or seawater can be scavenged through complexation with the carboxylate groups present within the CQD [59]. It was anticipated that these same groups would also coordinate other metal ions in a similar manner to that observed in previous metal–PAA systems [55–58]. Moreover, one could query whether a simple PAA film, with its abundance of carboxyl functionality, might be equally effective at removing metal ions. Nevertheless, the main strength of Mahmoud's work lies in the green credentials of the synthesis process and its relative simplicity—especially when considering the production of CQDs and their incorporation within polymer matrices.

Mohan et al. (2010) described the use of PAA to immobilize cobalt (II) cyclam (Co-Cy) complexes within a film [65]. In this case, the carboxylate groups of the anthranilic acid units were thought to form a coordinate bond with Co-Cy, transforming the latter into a mixed-ligand complex, with evidence suggesting a shift from its four-coordinate arrangement to an octahedral complex. When applied to an electrode, the PAA-Co-Cy composite was found to electrocatalyze the reduction of azidothymidine (AZT)—a potent antiviral drug used in the treatment of HIV. Nateghi and Fallahian (2007) employed a copolymer of pyrrole and anthranilic acid for the detection of copper ions [66]. Again, the carboxylate substituent played a pivotal role in the capture and preconcentration of the metal ion, thereby enabling its detection through electrochemical stripping techniques. It is clear that the anthranilic acid unit is extremely versatile in terms of being able to complex various transition metals for both catalytic and analytical purposes.

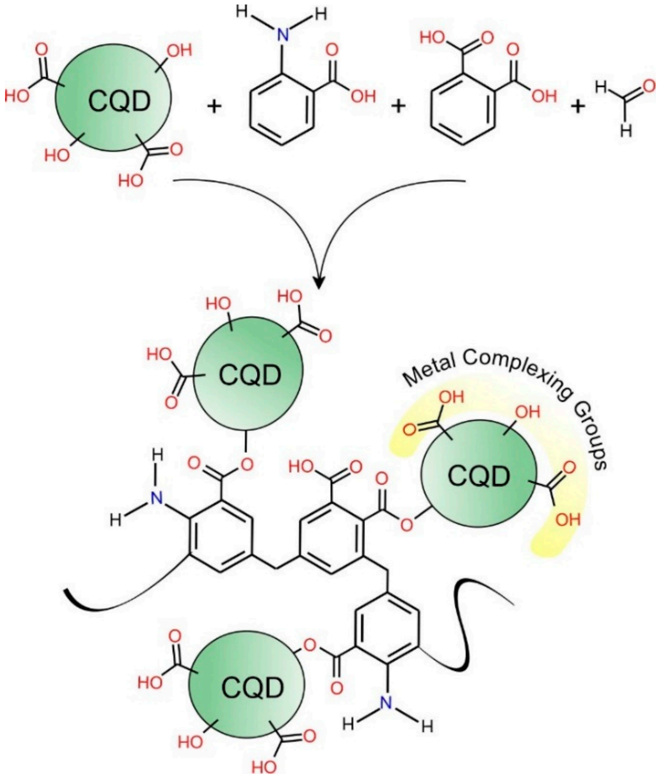

Figure 9. Condensation polymerization pathway incorporating anthranilic acid with carbon quantum dots (CQD), highlighting the metal ion complexing groups (adapted from [59]).

4.3. Corrosion Protection

Corrosion is a major issue in most industrial fields, and there continues to be extensive research into functional coatings that can minimize its effects. Coatings containing nitrogen, sulfur, and oxygen functionalities have been reported to be inhibitors, with those possessing unsaturated bond networks exhibiting higher efficiency [97]. More recently, attention has turned to the use of conducting polymers, wherein there is extensive delocalization of pi electrons. PANI and its derivatives have shown high inhibition efficiency toward mild steel in acidic conditions, but its processability, as noted previously, for coating surfaces can be problematic [98,99]. PAA can be imagined to be similarly effective, wherein the amino and carboxyl and the conjugated network could all play a part in the inhibition process. Banumathi and colleagues (2010) reported the use of a polyethylene glycol (PEG)–anthranilic acid composite for this purpose, with the PEG component presumably aiding the usability of the material [39]. Polymerization was oxidatively initiated using APS within a mixture of the two, but the actual composition of the composite was unclear. While APS will induce the polymerization and formation of PAA, the subsequent interaction with PEG has not been clarified.

Polyanthranilic-acid–metal composites (PAA-Zn, PAA-FE, PAA-Mg) were investigated by Sophia et al. (2010) as anti-corrosion films for stainless steel [40]. Chemical preparation of the composites was achieved through oxidation by either Fe(III) (PAA-Fe) or persulphate in the presence of either zinc oxide (PAA-Zn) or magnesium oxide (PAA-Mg). PAA-Fe and PAA-Zn were found to adhere strongly to the steel substrate with a granular texture and thereby served as an anti-corrosive pigment. PAA-Mg was not found to induce any significant improvement in inhibition over the PAA homopolymer. Shirazi et al. (2019) demonstrated the efficacy of a chemically prepared PANI-PAA copolymer in protecting stainless steel in an acid solution [41]. Different ratios of aniline/anthranilic acid were investigated, with an increasing concentration of anthranilic acid leading to increased solubility. The optimum composition was found to be a 3:0 PANI/PAA mixture, leveraging the majority of aniline for reduced solubility while effectively utilizing the carboxylate group of the anthranilic acid to strongly adsorb onto the metal [41]. The increased solubility of the high-PAA loading may explain the poor inhibition results observed by Sophia et al. (2010) with regard to the PAA homopolymer [40].

Lee and Kim (2018) examined the use of a PANI-PAA hybrid polymer as an anti-corrosion binder for silicon anodes for use within high-capacity Li ion batteries [37]. Silicon has been advocated as a replacement for the graphite electrodes that are presently used in Li batteries, as it has been reported to possess ten times the capacity of carbon material and should be sufficient for high-energy-density storage. Unfortunately, the subsequent charge–discharge cycles can induce dramatic volume changes in the silicon due to Li storage, and this can result in mechanical fracture and a rapid deterioration in battery efficiency and life cycle expectancy. Nano-structuring the silicon component to accommodate for the volume change through the use of nanowires, nanotubes, and networks has been proposed as a potential solution, but such solutions come with increased cost [100,101]. An alternative is to employ polymeric binders [100,102–104] to encase the electrode material, providing mechanical strength to the structure.

A number of conducting polymers (PANI, PEDOT, etc.) have been investigated as possible binders and have been proposed to provide the benefit of being an additional conducting element, which can increase the energy density through an increase in the active electrode material [100,103,104]. Despite many initial attempts, it was clear that most of the traditional systems engaged in, at best, only weak interactions with the Si surface. Polymers abundant in carboxylate functionalities, such as polyacrylic acid and alginate, have demonstrated an ability to hydrogen bond with the polar (OH) groups at the Si interface. Consequently, there have been endeavors to fabricate hybrid PANI–Polyacrylic acid composites, with PANI imparting electrical conductivity to the binding matrix. While PANI has no intrinsic groups capable of binding to Si, it could be envisaged that PANI-PAA hybrids would maximize the conductive backbone while exploiting the COOH groups within the anthranilic acid units to anchor the film to the Si electrode [39]. The greater solubility of the PANI-PAA composite could again be considered critical to ensuring complete coverage of the Si anode. Kim et al. (2020) polymerized aniline and anthranilic acid in the presence of chitosan to yield a chitosan–PANI–PAA composite [38]. In this case, it was suggested that the amino functionality of chitosan was directly incorporated into the PANI-PAA chains, leading to a grafted/crosslinked mesh. The polarity of chitosan was found to enhance water solubility and hence processing capability. Critically, the resulting 3D matrix, possessing an abundance of both amine and carboxylate functional groups, was found to strongly adsorb onto the Si surface. The conductive nature of the PANI-PAA copolymer component was attributed to a high initial capacity of 3057.3 mA h g^{-1}, with the 3D mesh binder allowing 51.4% retention after 300 cycles. The inexpensive nature of the PANI-PAA system, its water solubility, and its performance stand in marked contrast to the more conventional polyvinylidene fluoride (PVdF) coatings on Si and could have considerable implications for commercial Li ion battery production.

4.4. Electronic Devices

Memory devices based on conducting polymers have been proposed as an alternative to the conventional Si systems—offering scalability and low cost. While Si devices store information based on the amount of charge stored in a cell, the organic polymer approach relies upon changes in conductivity associated with an applied voltage. A resistive switching behavior has been observed with various metal–organic–metal sandwich structures, with high-performance devices being prototyped with thin films of PAA and PANI-PAA hybrids [51–53]. When constructed with Au, Al, or ITO electrodes, a bipolar memory characteristic was observed, which could be switched within a very low voltage range and, critically, typically exhibited a very high ON/OFF current ratio providing unambiguous registration of either state. Baek et al. (2007) used a self-doped polyanthranilic acid homopolymer exhibiting a very low current range (from 10^{-6} A to 10^{-11} A) dependent upon the applied voltage (1.6 V to −0.4 V) [52]. Upon conducting potential scanning up to −1.5 V, an electrical transition (ON) was found to occur at −0.5 V, leading to a dramatic change in current from 10^{-7} A to 10^{-3} A. The film could be returned to the OFF (low-conductivity) state by applying a voltage of +1.6 V. The ON/OFF current ratio was found to be in the 2.3×10^3–1.0×10^4 range (based on switching the applied voltages between −0.50 V and +1.60 V). These switching behaviors demonstrate that this device can be used as a nonvolatile memory device. The practical nature of the device was highlighted by the fact that the device's operation was unaffected by nitrogen or ambient air environments. These polymer devices were also shown to possess excellent electrical stability—with the ON state being retained for several months without degradation and with no degradation observed during the execution of repetitive write–read–erase functions [52]. It is noteworthy that Baek and colleagues did not observe any switching behavior exhibited by PANI homopolymer samples.

The use of PAA homopolymers has also been studied, with various combinations of mixed electrode systems for which the bottom electrode/top electrode configurations influencing the switching behavior between unipolar and bipolar responses were judiciously selected [51,52]. Baek and colleagues (2007) found that altering the device's design to one comprising two Au electrodes resulted in much better I–V switching properties than those involving a Au or Al top electrode and an ITO bottom electrode. In this case, the device exhibited similarly low current ranges (10^{-6} to 10^{-11} A) in the OFF state (between +0.84 V and –0.86 V), but these increased dramatically to 10^{-2} A at −0.87 V in the ON state. Here, the maximum ON/OFF ratio achieved was 1.0×10^5 [52]. While it is clear that conducting polymer systems have the capacity to serve as memory storage devices, processing capability must also be considered. Furthermore, the presence of the COOH substituent on the chain backbone and the solubility it imparts are key contributors to the success of PAA and PANI-PAA systems.

4.5. Molecular Grafting—Chemical/Biosensing

PANI lacks readily accessible functionality that enables covalent modification; hence, the great advantage of copolymerization with anthranilic acid lies in the ability to harness the abundance of carboxylate groups. These can be used as a facile means of tethering other molecular species to the film post polymerization. This is normally achieved using conventional EDC/NHS carbodiimide coupling procedures to activate the COOH group, preparing it for attack by an amino group from the proposed pendant molecule. The basic reaction scheme is highlighted in Figure 10. It is important to note that this approach has been successful in harnessing a variety of receptors—both chemical and biological.

Molecularly imprinted polymers (MIPs) have long been hailed as an effective chemical approach to biomolecular recognition and as an alternative to the more costly and complex antibody/aptamer systems. The premise of their design is based on a templating methodology in which functional monomers are polymerized around a target molecule. Removal of the latter should leave a cavity that is complementary in size and shape and that, ideally, will exhibit some affinity for the template molecule, thereby enabling its recognition and capture from a fresh solution. The electropolymerization of PANI-PAA in the presence of the target has been proposed as a simple means of imprinting Amlodipine (AML) and, in contrast to chemical polymerization methods, provides the added advantage of immobilizing the MIP directly upon the electrode surface [67]. Recognition of the AML target is achieved through hydrogen bond interactions between the amine and carboxylate groups of the PANI-PAA polymer and the oxygen–nitrogen groups on the AML. Detection was assessed through recovery experiments using human biofluids with good recoveries, and it could speculated that the polymer network, as well as enabling the capture of the AML, also served as a barrier to interferences and minimized the fouling effects of non-specific adsorption [70].

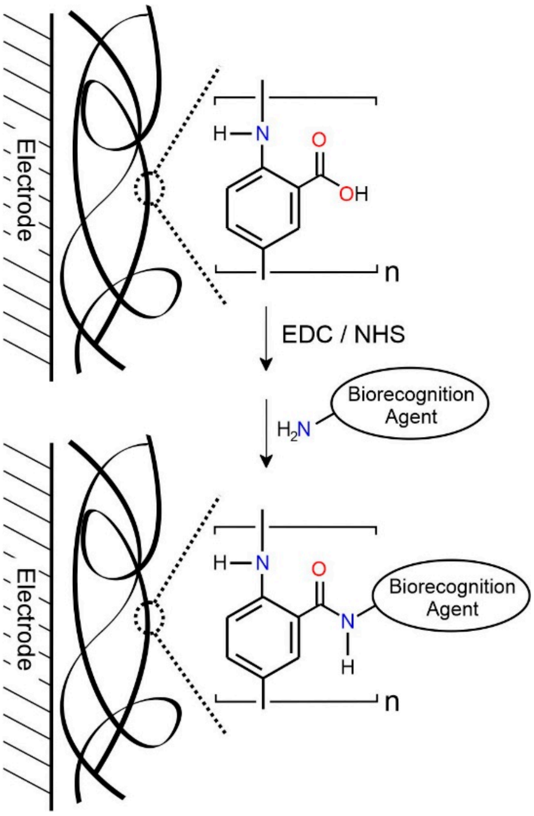

Figure 10. Post-polymerization modification through carbodiimide (EDC/NHS) coupling with a functional agent (complex, enzyme, antibody, or aptamer).

While the strategy devised by Hrichi and colleagues (2017) constitutes a relatively generic approach to MIP formation [67], an earlier approach by Gu et al. (2013) employed a more sophisticated system for dopamine detection involving the immobilization of functional groups possessing greater selectivity for the target [69]. In this case, 3-Aminophenylboronic acid was bound to a chemically polymerized PAN-PAA film through EDC/NHS carbodiimide coupling, as indicated in Figure 11A. It was envisaged that the subsequent attachment of the pendant B(OH)2 groups would be capable of reversibly binding dopamine. The formation of stable cyclic esters between boronic acid groups and 1,2-diols is well known. Template release in this case was achieved through the facile electrochemical oxidation of the boronic-acid-bound dopamine to the corresponding 1,2-quinone species (Figure 11B). Here, the COOH group of the PAA component was critical in enabling the processability of the polymer network as well as in providing a covalent tether for the attachment of the boronic acid group. The covalent imprinting process adopted by Gu and colleagues is reported to allow a more homogeneous distribution of binding sites through the combination of specific (cyclic ester) functionality and electrostatic/H bonding providing cavities with better selectivity over the simpler electro-polymerized templating system.

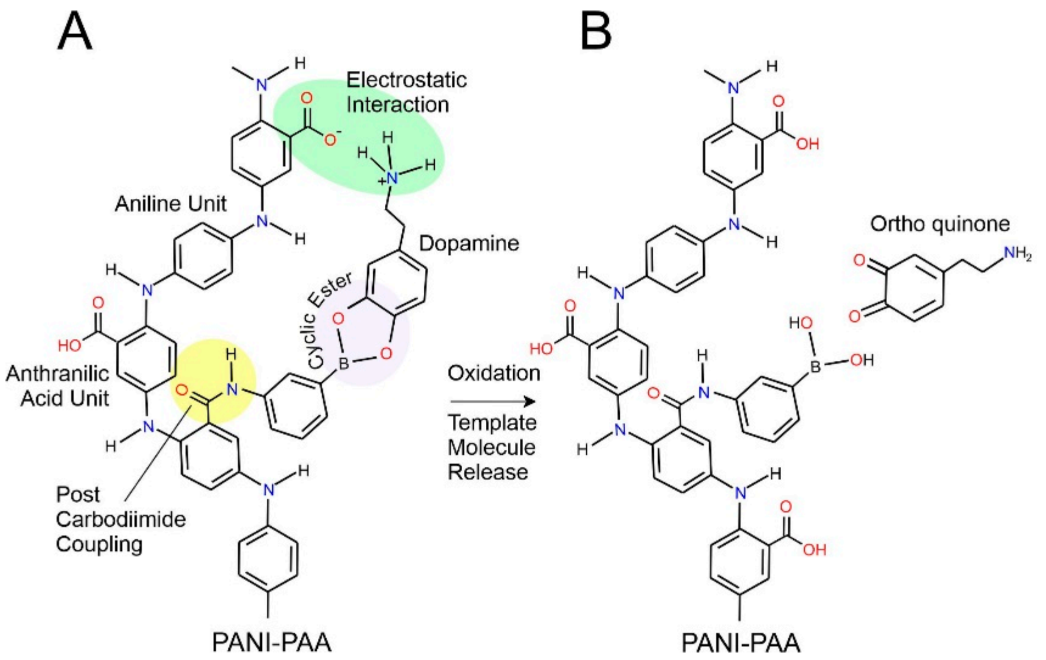

Figure 11. Poly(aniline-co-anthranilic acid) (PANI-PAA) polymer, highlighting the direct interaction with boronic acid groups and indirect electrostatic interactions enhancing the molecular recognition of dopamine.

Gopalan et al. (2016) used a highly sophisticated composite assembly based on a grafted PAN-PAA copolymer as a non-enzymatic sensor for glucose [69]. Their team functionalized graphene nanobeads with PANI-PAA through chemical oxidation (via APS) and then tethered a polyethyleneimine (PEI) linker via EDC/NHS linkage, as previously indicated in Figure 10. In contrast to the carboxyl groups on most PAA functional interfaces, modification with PEI provided an abundance of terminal amines (R-NH_2), which were used to capture ferrocene redox probes (through Schiff base reactions of the carboxaldehyde derivative). A further step involved the electrodeposition of Cu nanoparticles, which were responsible for the detection of glucose, where the latter is chemically oxidized by Cu(II) ions. The network of ferrocene redox moieties in this case aids the electron transfer process, and the sensor was shown to perform well in human serum.

EDC/NHS coupling has been used extensively in biosensor development, wherein the lysine resides within the protein shell of enzymes and antibodies can be covalently linked to a carboxylate functionalized polymer. These approaches have been comprehensively reviewed elsewhere [101,105,106]. A summary of the biocomponents anchored to PAA-based systems is presented in Table 2.

In the case of antibody and aptamer systems, the PAA or PANI-PAA film is commonly electropolymerized and serves only as a suitable support for the subsequent immobilization of the recognition component. Talet et al. (2013) employed such a methodology, in which antibodies for Cancer Antigen 125 (CA125) were immobilized on a PAA film on a graphite screen-printed electrode and detected using a label-free methodology [77]. Here, the detection principle was initially based on monitoring the changes in the interfacial property that arises between the electrode surface and solution when a binding event occurs between the antibody and target antigen. Detection of the binding event was achieved using electrochemical impedance spectroscopy (EIS) with a ferrocyanide–ferricyanide redox probe, with a linear response observed between 0 and 50 U/mL and a detection limit (LOD) of 7.6 U/mL. Taleat and colleagues attempted to improve this approach using a sandwich strategy in which the secondary antibodies were conjugated to gold nanoparticles (AuNP). In this approach, a silver solution was introduced post binding, with the reaction between AuNP and Ag+ leading to the generation of AgNPs, which could be electrochemically quantified through stripping voltammetry. This led to an enhancement in the LOD for

CA125 amounting to 2 U/mL. Similar strategies were employed for the antibody-based detection of Tumor Necrosis Factor α, with PAA again used as a convenient electropolymerizable substrate for subsequent modification [78].

Table 2. Sensor systems exploiting polyanthranilic acid as an immobilization substrate.

Polymer Type	Substrate	Agent	Target Biomarker	Immobilization Method	Ref.
PAA	CPE/Pt	Co(II)–cyclam	Azidothymidine	Complexation	[65]
PANI-PAA	GCE	3-Amino-boronic Acid	Dopamine	EDC	[68]
PP/PAA	Pt	GOx	Glucose	GA	[70]
PAA	CFME	Laccase	p-nonylphenol	EDC	[71]
PEDOT/PAA	Pt	Gox	Glucose	EDC	[72]
PANI-PAA	Multiwell Plate	GOx, HRP, Tyrosinase	H_2O_2, Glucose, catechol	EDC	[73]
P(AA-coCNTA)-PVAc	ESF	GOx	Glucose	EDC	[74]
PAcN/PU/PAA	ESF	Tyrosinase	N/A	EDC	[75]
P(AA-co CNTA)	ESF	Tyrosinase			[76]
PAA	GSPE	Antibody	Tumor Necrosis Factor α	EDC	[77]
PAA	GSPE	Antibody	CA 125	EDC	[78]
PANI-PAA	GSPE	Aptamer	β-lactoglobulin	EDC	[79]
PANI-PAA	GSPE	Aptamer	Aflatoxin B1	EDC	[80]

PAA = polyanthranilic acid; PANI = polyaniline; PP = polypyrrole; PEDOT = Poly(3,4-ethylenedioxythiophene); PAcN = polyacrylonitrile; PU = polyurethane; P(AA-co-CNTA) = Poly(anthranilic acid-co-3-carboxy-N-(2-thenylidene)aniline); PVAc = poly vinyl acetate; ESF = electrospun fiber; CPE = carbon paste electrode; GSPE = graphite screen-printed fiber; CFE; carbon fiber mat electrode; EDC = 1-Ethyl-3-(3′-dimethylaminopropyl) carbodiimide hydrochloride; GA = glutaraldehyde; GOx = glucose oxidase; HRP = horseradish peroxidase; GC = glassy carbon electrode.

Lettieri et al. (2020) developed a competitive aptamer assay for b-lactoglobulin (BLG) [79]. The recognition and capture of a biotin-labelled BLG allowed the subsequent binding of a streptavidin-alkaline phosphate conjugate, with electrochemical detection achieved through the enzyme hydrolysis of 1-nphthyl-phosphate to 1-naphthol. The greater the concentration of BLG in the sample, the greater the proportion of aptamer sites that became occupied. As a consequence, the proportion of biotin-labelled BLG was captured, and, likewise, fewer enzyme conjugates were generated, leading to a decrease in the generation of 1-naphthol. A similar methodology was employed by Selvolinia et al. (2019) for the detection of Alfatoxin, highlighting the generic nature of this approach [80].

Rather than using PAA for its immobilization capabilities, Berkkan et al. (2010) employed a copolymer consisting of pyrrole and anthranilic acid in order to harness its interference rejection properties [70]. While the previous discussions have lauded the capability of anthranilic acid components to pick up metal ions through interaction with the carboxyl functionality [55–58], the latter can also be useful for the electrostatic repulsion of similarly charged interferences. In this respect, the PAA component is employed as an electropolymerizable variant of Nafion® in order to exclude anionic species, such as ascorbate or urate, which would normally lead to significant interference for conventional electrochemical enzyme sensors. In contrast to the previous use of EDC/NHS linkage for the immobilization of the biocomponent, Berkkan and colleagues used glutaraldehyde to chemically crosslink the enzyme. This preserved the carboxylate functionality of the underlying PAA, which would otherwise have been compromised through carbodiimide bonding, and retained the anti-interferent anionic interface (COO-). While PANI-PAA films have typically been used only as the underpinning support, it is worth noting that these films retain permeability to small molecular species. This can be attributed to the steric considerations of the COOH within the anthranilic acid units increasing interchain separation at the time of polymerization.

5. Conclusions

Anthranilic acid was initially regarded as a useful monomer for altering the solubility of polyaniline copolymers and can greatly improve their processing capability. While these are significant merits, it must be recognized that the monomer unit can bestow considerably more. Retaining electroactivity beyond pH 4 through self-doping greatly expands its use as a copolymer or homopolymer for electronic applications. Moreover, the carboxylate group serves as a key attachment site, opening up a vast array of sensing opportunities. Recognition elements such as enzymes, antibodies, or aptamers can be easily anchored and enable the detection of target elements by taking advantage of the intrinsic conductivity of the underlying polymer framework. At the smaller scales, there continues to be substantial progress in the development of nanomaterials for biosensing applications, and yet it is clear that there is ample scope for using polyanthranilic acid as a both a means of templating catalytic particles and as a core–shell coating. In the latter application, gold has often served as a key substrate, but it frequently requires modification in order to host receptors. The use of anthranilic acid provides opportunities for the creation of the central catalytic particle whilst simultaneously decorating and priming the external surface for the subsequent attachment of the biological or chemical receptor. On the macro scale, chemical synthesis of the copolymer is relatively facile, promoting scalability, while the increased solubility of the polymer provides routes for conventional processing. When the latter is combined with anthranilic acid's capability to template catalytic nanoparticles, there could be a host of opportunities for electrosynthesis. It is evident that even though anthranilic acid has served more as an academic curiosity, it holds considerable industrial promise. Its low cost, ease of production, and intrinsic chemical versatility could open many avenues for exploration.

While the number of papers relating to conducting polymers continues to grow, it can appear, at least based on the superficial inspection provided earlier, that the use of polyaniline and polypyrrole is beginning to plateau. One possible factor in this trend is that there is increasing interest in more functional polymers that can be directly tailored to particular applications. Both polyaniline and polypyrrole, while robust, are chemically inflexible. They lack any readily accessible means of chemical modification, hence the need for new derivatives that can be better tuned. It is here that anthranilic acid could come to the fore, offering ease of copolymerization with existing polymer systems (polyaniline, polypyrrole, pedot, etc.) and providing a carboxylate group that can be readily exploited for post-film modification and thereby greatly expanding the functionality of the polymer.

Author Contributions: Conceptualization, J.D., P.P. and R.B.S.; methodology, J.D.; formal analysis, R.M. (Rachel McCormick); investigation, R.M. (Rachel McCormick), E.B., P.J.D., V.G. and R.M. (Regan McMath); resources, J.D. and P.P.; data curation, R.M. (Rachel McCormick), V.G. and R.M. (Regan McMath), J.D.; writing—original draft preparation, J.D., R.B.S. and R.M. (Rachel McCormick); writing—review and editing, J.D., P.P. and R.B.S.; visualization, J.D. and V.G.; supervision, J.D. and P.P.; project administration, J.D. and P.P.; funding acquisition, J.D. and P.P. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Department for the Economy (DfE) Northern Ireland.

Data Availability Statement: Data relating to Figure 1 are available on request. No other new data were generated.

Conflicts of Interest: The authors declare no conflicts of interest, and the funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript; or in the decision to publish the results.

References

1. Shirakawa, H.; Louis, E.J.; MacDiarmid, A.G.; Chiang, C.K.; Heeger, A.J. Synthesis of electrically conducting organic polymers: Halogen derivatives of polyacetylene, (CH)x. *Chem. Soc. Chem. Commun.* **1977**, 578–580. [CrossRef]
2. Tundwal, A.; Kumar, H.; Binoj, B.J.; Sharma, R.; Kumar, G.; Kumari, R.; Dhayal, A.; Yadav, A.; Singh, D.; Kumar, P. Developments in conducting polymer-, metal oxide-, and carbon nanotube-based composite electrode materials for supercapacitors: A review. *RSC Adv.* **2024**, *14*, 9406. [CrossRef] [PubMed]
3. Nguyen, T.V.; Le, Q.V.; Peng, S.; Dai, Z.; Ahn, S.H.; Kim, S.Y. Exploring Conducting Polymers as a Promising Alternative for Electrochromic Devices, Adv. *Mater. Technol.* **2023**, *8*, 2300474.
4. Yi, H.; Patel, R.; Patel, K.D.; Bouchard, L.-S.; Jha, A.; Perriman, A.W.; Patel, M. Conducting polymer-based scaffolds for neuronal tissue engineering. *J. Mater. Chem. B* **2023**, *11*, 11006. [CrossRef] [PubMed]
5. Zhang, P.; Zhu, B.; Du, P.; Travas-Sejdic, J. Electrochemical and Electrical Biosensors for Wearable and Implantable Electronics Based on Conducting Polymers and Carbon-Based Materials. *Chem. Rev.* **2024**, *124*, 722–767. [CrossRef] [PubMed]
6. Le, C.V.; Yoon, H. Advances in the Use of Conducting Polymers for Healthcare Monitoring. *Int. J. Mol. Sci.* **2024**, *25*, 1564. [CrossRef] [PubMed]
7. Tundwal, A.; Kumar, H.; Binoj, B.J.; Sharma, R.; Kumari, R.; Yadav, A.; Kumar, G.; Dhayal, A.; Yadav, A.; Singh, D.; et al. Conducting polymers and carbon nanotubes in the field of environmental remediation: Sustainable developments. *Coord. Chem. Rev.* **2024**, *500*, 215533. [CrossRef]
8. Rasmussen, S.C. The Early History of Polyaniline: Discovery and Origins. *Substantia* **2017**, *1*, 99–109.
9. Namsheer, K.; Rout, C.K. Conducting polymers: A comprehensive review on recent advances in synthesis, properties and applications. *RSC Adv.* **2021**, *11*, 5659–5697.
10. Babel, V.; Hiran, B.L. A review on polyaniline composites: Synthesis, characterization, and applications. *Polym. Compos.* **2021**, *42*, 3142–3157. [CrossRef]
11. Bhadra, J.; Alkareem, A.; Al-Thani, N. A review of advances in the preparation and application of polyaniline based thermoset blends and composites. *J. Polym. Res.* **2020**, *27*, 122. [CrossRef]
12. Liao, G.; Li, Q.; Xu, Z. The chemical modification of polyaniline with enhanced properties: A review. *Prog. Org. Coat.* **2019**, *126*, 35–43. [CrossRef]
13. Beygisangchin, M.; Abdul Rashid, S.; Shafie, S.; Sadrolhosseini, A.R.; Lim, H.N. Preparations, Properties, and Applications of Polyaniline and Polyaniline Thin Films—A Review. *Polymers* **2021**, *13*, 2003. [CrossRef]
14. Eskandari, E.; Kosari, M.; Farahani, M.H.D.A.; Khiavi, N.D.; Saeedikhani, M.; Katal, R.; Zarinejad, M. A review on polyaniline-based materials applications in heavy metals removal and catalytic processes. *Sep. Purif. Technol.* **2020**, *231*, 115901. [CrossRef]
15. Talukder, M.; Khan, M.M.R.; Amin, K. A review on polyaniline (PANI) based nanocomposites for water purification. *S. Afr. J. Chem. Eng.* **2023**, *44*, 276–282. [CrossRef]
16. Sen, T.; Mishra, S.; Shimpi, N.G. Synthesis and sensing applications of polyaniline nanocomposites: A review. *RSC Adv.* **2016**, *6*, 42196–42222. [CrossRef]
17. Zare, E.N.; Makvandi, P.; Ashtari, B.; Rossi, F.; Motahari, A.; Perale, G. Progress in Conductive Polyaniline-Based Nanocomposites for Biomedical Applications: A Review. *J. Med. Chem.* **2020**, *63*, 1–22. [CrossRef]
18. Ogura, K.; Shiigi, H.; Nakayama, M.; Ogawa, A. Thermal Properties of Poly(anthranilic acid) (PANA) and Humidity-Sensitive Composites Derived from Heat-Treated PANA and Poly(vinyl alcohol). *J. Polym. Sci. Part. A Polym. Chem.* **1999**, *37*, 4458–4465. [CrossRef]
19. Wang, Y.; Knoll, W. In situ electrochemical and surface plasmon resonance (SPR) studies of aniline-carboxylated aniline copolymers. *Anal. Chim. Acta* **2006**, *558*, 150–157. [CrossRef]
20. Shan, D.; Mu, S. Electrochemical characteristics of polyaniline synthesized in the presence of ferrocene sulfonic acid. *Synth. Met.* **2002**, *126*, 225–232. [CrossRef]
21. Khan, M.; Answer, T.; Mohammad, F. Sulphonated polyaniline/MWCNTs nanocomposite: Preparation and promising thermoelectric performance. *Int. Nano Lett.* **2018**, *8*, 213–220. [CrossRef]
22. Li, C.; Mu, S. Electrochromic properties of sulfonic acid ring-substituted polyaniline in aqueous and non-aqueous media. *Synth. Met.* **2004**, *144*, 143–149. [CrossRef]
23. Amaya, T.; Abe, Y.; Inada, Y.; Hirao, T. Synthesis of self-doped conducting polyaniline bearing phosphonic acid. *Tetrahedron Lett.* **2014**, *55*, 3976–3978. [CrossRef]
24. Benyoucef, A.; Huerta, F.; Vazquez, J.L.; Morallon, E. Synthesis and in situ FTIRS characterization of conducting polymers obtained from aminobenzoic acid isomers at platinum electrodes. *Eur. Polym. J.* **2005**, *41*, 843–852. [CrossRef]
25. Melad, O. Co and Ter Polymerization of Poly(o-anthranilic acid): Synthesis and Characterization. *Polym. Sci. Ser. B* **2015**, *57*, 669–676. [CrossRef]
26. Al-Hussaini, A.S.; Zoromba, M.S.; El-Ghamaz, N.A. In Situ Polymerization and Characterization of Aniline and O-Anthranilic Acid Copolymer/Pyrogenic Silica Nanocomposites. *Polym.-Plast. Technol. Eng.* **2013**, *52*, 1089–1096. [CrossRef]
27. Sushchenko, I.G.; Meleshko, T.K.; Gofman, I.V.; Sukhanova, T.E.; Vylegzhanina, M.E.; Abalov, I.V.; Vlasova, E.N.; Popova, E.N.; Yudin, V.E.; Yakimanskii, A.V. Film Composites of Polyimide with Polyaniline and Poly(aniline-co-anthranilic acid). *Polym. Sci. Ser. A* **2011**, *53*, 800–810. [CrossRef]

28. Al-Hussaini, A.S. Inexpensive Fabrication and Characterization of Crystalline Poly(o-Anthranilic Acid-co-o-Phenylenediamine) Emeraldine Base/Bentonite Nanocomposites. *Polym.-Plast. Technol. Eng.* **2016**, *55*, 1386–1392. [CrossRef]
29. Dash, M.P.; Tripathy, M.; Sasmal, A.; Mohanty, G.C.; Nayak, P.L. Poly(anthranilic acid)/multi-walled carbon nanotube composites: Spectral, morphological, and electrical properties. *J. Mater. Sci.* **2010**, *45*, 3858–3865. [CrossRef]
30. Al-Hussaini, A.S.; Zoromba, M.S. New Crystalline Aniline and o-Anthranilic Acid Copolymer/Kaolinite Composites. *Polym.-Plast. Technol. Eng.* **2014**, *53*, 1021–1027. [CrossRef]
31. Ayad, M.M.; Salahuddin, N.A.; Abou-Seif, A.K.; Alghaysh, M.O. Chemical synthesis and characterization of aniline and o-anthranilic acid copolymer. *Eur. Polym. J.* **2008**, *44*, 426–435. [CrossRef]
32. Al-Hussaini, A.S. New polymeric based materials: Terpoly (aniline, diphenyl amine, and o-anthranilic acid)/kaolinite composites. *Polym. Adv. Technol.* **2016**, *27*, 1604–1608. [CrossRef]
33. Wu, M.-S.; Wen, T.-C.; Gopalana, A. Electrochemical Copolymerization of Diphenylamine and Anthranilic Acid with Various Feed Ratios. *J. Electrochem. Soc.* **2001**, *148*, D65–D73. [CrossRef]
34. Nateghi, M.R.; Borhani, M. Preparation, characterization and application of poly anthranilic acid-co-pyrrole. *React. Funct. Polym.* **2008**, *68*, 153–160. [CrossRef]
35. Al-Hussaini, A.S. Modified Nonconventional Synthesis of New Terpoly(Aniline, o-Anthranilic Acid and o-Phenylenediamine)/Bentonite Composites. *Polym.-Plast. Technol. Eng.* **2015**, *54*, 61–67. [CrossRef]
36. Mokhtar, H.I.; Abdel-Salam, R.A.; Hadad, G.M. Nanocomposite of silica coated magnetite nanoparticles and aniline-anthranilic acid co-polymeric nanorods with improved stability and selectivity for fluoroquinolones dispersive micro solid phase extraction. *J. Chromatogr. B* **2022**, *1206*, 123350. [CrossRef] [PubMed]
37. Lee, K.; Kim, T.-H. Poly(aniline-co-anthranilic acid) as an electrically conductive and mechanically stable binder for high-performance silicon anodes. *Electrochim. Acta* **2018**, *283*, 260–268. [CrossRef]
38. Kim, E.; Rajeev, K.K.; Nam, J.; Mun, J.; Kim, T.-Y. Chitosan-grafted-poly(aniline-co-anthranilic acid) as a water soluble binder to form 3D structures for Si anodes. *RSC Adv.* **2020**, *10*, 7643. [CrossRef] [PubMed]
39. Banumathi, N.; Subhashini, S.; Rajalakshmi, R. Polyethelene Glycol-Anthranilic Acid Composite as Corrosion Inhibitor for Mild Steel in Acid Medium. *E-J. Chem.* **2010**, *7*, S67–S72. [CrossRef]
40. Sophia, I.A.; Gopu, G.; Vedhi, C. Synthesis and Characterization of Poly Anthranilic Acid Metal Nanocomposites. *Open J. Synth. Theory Appl.* **2012**, *1*, 1–8. [CrossRef]
41. Shirazi, Z.; Keshavarz, M.H.; Golikand, A.N.; Esmaeilpour, K. Corrosion Inhibition of Stainless Steel in HCl Solution Using Newly Aniline and o-Anthranilic Acid Copolymer. *Prot. Met. Phys. Chem. Surf.* **2019**, *55*, 795–802. [CrossRef]
42. Mallick, K.; Mondal, K.; Witcomb, M.; Scurrell, M. Gas phase hydrogenation reaction using a 'metal nanoparticle–polymer' composite catalyst. *J. Mater. Sci.* **2008**, *43*, 6289–6295. [CrossRef]
43. Ros, T.G.; van Dillen, A.J.; Geus, J.W.; Koningsberger, D.C. Modification of Carbon Nanofibres for the Immobilization of Metal Complexes: A Case Study with Rhodium and Anthranilic Acid. *Chem. Eur. J.* **2002**, *8*, 2868–2878. [CrossRef] [PubMed]
44. Al-Hussaini, A.S.; Eltabie, K.R.; Rashad, M.E.E. One-pot modern fabrication and characterization of TiO_2@terpoly(aniline, anthranilic acid and o-phenylenediamine) coreshell nanocomposites via polycondensation. *Polymer* **2016**, *101*, 328–337. [CrossRef]
45. Chao, D.; Lu, X.; Chen, J.; Zhang, W.; Wei, Y. Anthranilic Acid Assisted Preparation of Fe_3O_4–Poly(aniline-co-o-anthranilic acid) Nanoparticles. *J. Appl. Polym. Sci.* **2006**, *102*, 1666–1671. [CrossRef]
46. Zoromba, M.S.; El-Ghamaz, N.A. Electrical conduction and dielectric properties of doped iron/poly(aniline-co-o-anthranilic acid) copolymer and production of magnetite-hematite nanoparticles based on composites as precursor. *Mater. Express* **2016**, *6*, 414–422. [CrossRef]
47. Jayakrishnan, P.; Ramesan, M.T. Synthesis, structural, magnetoelectric and thermal properties of poly (anthranilic acid)/magnetite nanocomposites. *Polym. Bull.* **2017**, *74*, 3179–3198. [CrossRef]
48. Jayakrishnan, P.; Ramesan, M.T. Temperature Dependence of the Electrical Conductivity of Poly(Anthranilic Acid)/Magnetite Nanocomposites and the Applicability of Different Conductivity Models. *Polym. Compos.* **2018**, *39*, 2791–2800. [CrossRef]
49. Zoromba, M.S.; Al-Hossainy, A.F.; Abdel-Aziza, M.H. Conductive thin films based on poly (aniline-co-o-anthranilic acid)/magnetite nanocomposite for photovoltaic applications. *Synth. Met.* **2017**, *231*, 34–43. [CrossRef]
50. Hosny, M.M.; Abdel-Aziz, M.H.; Zoromba, M.S.; Al-Hossainy, A.F. Design and synthesis of high-performance polymer blend solar cell. *J. Mater. Res. Technol.* **2024**, *28*, 4199–4211. [CrossRef]
51. Lee, D.; Baek, S.; Ree, M.; Kim, O. Novel Resistance Switching Devices Based on Sub-10nm Polymer Thin Film. *Jpn. J. Appl. Phys.* **2008**, *47*, 5665–5667. [CrossRef]
52. Baek, S.; Lee, D.; Kim, J.; Hong, S.-H.; Kim, O.; Ree, M. Novel Digital Nonvolatile Memory Devices Based on Semiconducting Polymer Thin Films. *Adv. Funct. Mater.* **2007**, *17*, 2637–2644. [CrossRef]
53. Nam, S.; Ko, Y.-G.; Hahm, S.G.; Park, S.; Seo, J.; Lee, Y.; Kim, H.; Ree, M.; Kim, Y. Organic nonvolatile memory transistors with self-doped polymer energy well structures. *NPG Asia Mater.* **2013**, *5*, e33. [CrossRef]
54. Cho, W.; Park, S.-J.; Kim, S. Effect of monomer concentration on interfacial synthesis of platinum loaded polyaniline nanocomplex using poly(styrenesulfonic acid). *Synth. Met.* **2011**, *161*, 2446–2450. [CrossRef]
55. Hosny, N.M.; Nowesser, N.; Al-Hussaini, A.S.; Zoromba, M.S. Doped copolymer of polyanthranilic acid and o-aminophenol (AA-co-OAP): Synthesis, spectral characterization and the use of the doped copolymer as precursor of α-Fe_2O_3 nanoparticles. *J. Mol. Struct.* **2016**, *1106*, 479–484. [CrossRef]

56. Hosny, N.M.; Al-Hussaini, A.S.; Nowesser, N.; Zoromba, M.S. Effect of inclusion of some transition metal ions and use of the doped polymer in synthesizing α-Fe_2O_3 nanoparticles via thermal decomposition rout. *J. Therm. Anal. Calorim.* **2016**, *124*, 287–293. [CrossRef]
57. Hosny, N.M.; Badr, M.; El-Dossoki, F.I. Copolymer of m-phenylenediamine and anthranilic acid (P(mPDA-co-AA): New precursor of MnO Nanoparticles. *Polym.-Plast. Technol. Mater.* **2019**, *58*, 1178–1190. [CrossRef]
58. Al-Hossainy, A.F.; Bassyouni, M.; Zoromba, M.S. Elucidation of Electrical and Optical Parameters of Poly(o-anthranilic acid)-poly(o-amino phenol)/Copper Oxide Nanocomposites Thin Films. *J. Inorg. Organomet. Polym. Mater.* **2018**, *28*, 2572–2583. [CrossRef]
59. Mahmoud, M.E.; Fekry, N.A.; Abdelfattah, A.M. Removal of uranium (VI) from water by the action of microwave-rapid green synthesized carbon quantum dots from starch-water system and supported onto polymeric matrix. *J. Hazard. Mater.* **2020**, *397*, 122770. [CrossRef]
60. Han, D.; Song, J.; Ding, X.; Xu, X.; Niu, L. Fabrication and characterization of self-doped poly (aniline-co-anthranilic acid) nanorods in bundles. *Mater. Chem. Phys.* **2007**, *105*, 380–384. [CrossRef]
61. Gupta, B.; Melvin, A.; Prakash, R. Synthesis of polyanthranilic acid–Au nanocomposites by emulsion polymerization: Development of dopamine sensor. *Bull. Mater. Sci.* **2014**, *37*, 1389–1395. [CrossRef]
62. Al-Hussaini, A.S.; Abdel-Hameed, E.M.; Hassan, M.E.R. Synthesis of Smart Core-shell Nanocomposites with Enhanced Photocatalytic Efficacy. *Polym.-Plast. Technol. Mater.* **2020**, *59*, 1956–1966. [CrossRef]
63. Golshaei, R.; Guler, Z.; Ünsal, C.; Sarac, A.S. In situ spectroscopic and electrochemical impedance study of gold/poly (anthranilic acid) core/shell nanoparticles. *Eur. Polym. J.* **2015**, *66*, 502–512. [CrossRef]
64. Al-Hussaini, A.S.; El-Bana, W.E.; El-Ghamaz, N.A. New semiconductor core-shell based on nano-rods core materials. *Polym.-Plast. Technol. Mater.* **2020**, *59*, 630–641. [CrossRef]
65. Mohan, S.; Prakash, R. Novel conducting polymer functionalized with metal–cyclam complex and its sensor application: Development of azidothymidine drug sensor. *Talanta* **2010**, *81*, 449–454. [CrossRef] [PubMed]
66. Nateghi, M.R.; Fallahian, M.H. Self-doped Anthranilic Acid-Pyrrole Copolymer/Gold Electrodes for Selective Preconcentration and Determination of Cu(I) by Differential Pulse Anodic Stripping Voltammetry. *Anal. Sci.* **2007**, *23*, 563–567. [CrossRef] [PubMed]
67. Hrichi, H.; Monser, L.; Adhoum, N. A novel electrochemical sensor based on electropolymerized molecularly imprinted poly(aniline-co-anthranilic acid) for sensitive detection of amlodipine. *J. Electroanal. Chem.* **2017**, *805*, 133–145. [CrossRef]
68. Gu, L.; Jiang, X.; Liang, Y.; Zhou, T.; Shi, G. Double recognition of dopamine based on a boronic acid functionalized poly(aniline-co-anthranilic acid)–molecularly imprinted polymer composite. *Analyst* **2013**, *138*, 5461. [CrossRef] [PubMed]
69. Gopalan, A.I.; Muthuchamy, N.; Komathi, S.; Lee, K.-P. A novel multicomponent redox polymer nanobead based high performance non-enzymatic glucose sensor. *Biosens. Bioelectron.* **2016**, *84*, 53–63. [CrossRef]
70. Berkkan, A.; Seçkin, A.I.; Pekmez, K.; Tamer, U. Amperometric enzyme electrode for glucose determination based on poly(pyrrole-2-aminobenzoic acid). *J. Solid. State Electrochem.* **2010**, *14*, 975–980. [CrossRef]
71. Jose, S.; Thadathil, D.A.; Ghosh, M.; Varghese, A. Enzyme immobilized conducting polymer-based biosensor for the electrochemical determination of the eco-toxic pollutant p-nonylphenol. *Electrochim. Acta* **2023**, *460*, 142591. [CrossRef]
72. Krzyczmonik, P.; Socha, E.; Skrzypek, S. Immobilization of glucose oxidase on modified electrodes with composite layers based on poly(3,4-ethylenedioxythiophene). *Bioelectrochemistry* **2015**, *101*, 8–13. [CrossRef]
73. Hosu, O.; Lettieri, M.; Papara, N.; Ravalli, A.; Sandulescu, R.; Cristea, C.; Marrazza, G. Colorimetric multienzymatic smart sensors for hydrogen peroxide, glucose and catechol screening analysis. *Talanta* **2019**, *204*, 525–532. [CrossRef]
74. Golshaei, R.; Karazehir, T.; Ghoreishi, S.M.; Ates, M.; Sarac, A.S. Glucose oxidase immobilization onto Au/poly[anthranilic acid-co-3-carboxy-N-(2-thenylidene)aniline]/PVAc electrospun nanofibers. *Polym. Bull.* **2017**, *74*, 1493–1517. [CrossRef]
75. Dagli, U.; Guler, Z.; Sarac, A.S. Covalent Immobilization of Tyrosinase on Electrospun Polyacrylonitrile/Polyurethane/Poly(m-anthranilic acid) Nanofibers: An Electrochemical Impedance Study. *Polym.-Plast. Technol. Eng.* **2015**, *54*, 1494–1504. [CrossRef]
76. Golshaei, R.; Gokce, Z.G.; Ghoreishi, S.M.; Sarac, A.S. Au/PANA/PVAc and Au/P(ANA-co-CNTA)/PVAc electrospun nanofibers as tyrosinase immobilization supports. International Journal of Polymeric Materials and Polymeric. *Biomaterials* **2017**, *66*, 658–668.
77. Taleat, Z.; Ravalli, A.; Mazloum-Ardakani, M.; Marrazza, G. CA 125 Immunosensor Based on Poly-Anthranilic Acid Modified Screen-Printed Electrodes. *Electroanalysis* **2013**, *25*, 269–277. [CrossRef]
78. Mazloum-Ardakani, M.; Hosseinzadeh, L.; Taleat, Z. Two kinds of electrochemical immunoassays for the tumor necrosis factor α in human serum using screen-printed graphite electrodes modified with poly (anthranilic acid). *Microchim. Acta.* **2014**, *181*, 917–924. [CrossRef]
79. Lettieri, M.; Hosu, O.; Adumitrachioaie, A.; Cristea, C.; Marrazza, G. Beta-lactoglobulin Electrochemical Detection Based with an Innovative Platform Based on Composite Polymer. *Electroanalysis* **2020**, *32*, 217–225. [CrossRef]
80. Selvolini, G.; Lettieri, M.; Tassoni, L.; Gastaldello, S.; Grillo, M.; Maran, C.; Marrazza, G. Electrochemical enzyme-linked oligonucleotide array for aflatoxin B1 detection. *Talanta* **2019**, *203*, 49–57. [CrossRef]
81. Zoromba, M.S.; Ismail, M.I.M.; Bassyouni, M.; Abdel-Aziz, M.H.; Salah, N.; Alshahrie, A.; Memic, A. Fabrication and characterization of poly (aniline-co-o-anthranilic acid)/magnetite nanocomposites and their application in wastewater treatment. *Colloids Surf. A Physicochem. Eng. Asp.* **2017**, *520*, 121–130. [CrossRef]

82. Pawlowski, T.; Pawlak, D.; Inglot, M.; Zalewska, M.; Marciniak, D.; Bugajska, J.; Janocha-Litwin, J.; Malyszczak, K. The role of anthranilic acid in the increase of depressive symptoms and major depressive disorder during treatment for hepatitis C with pegylated interferon-α2a and oral ribavirin. *J. Psychiatry Neurosci.* **2021**, *46*, E166. [CrossRef] [PubMed]
83. Shaw, C.; Hess, M.; Weimer, B.C. Microbial-Derived Tryptophan Metabolites and Their Role in Neurological Disease: Anthranilic Acid and Anthranilic Acid Derivatives. *Microorganisms* **2023**, *11*, 1825. [CrossRef] [PubMed]
84. Song, S.; Yin, W.; Sun, X.; Cui, B.; Huang, L.; Li, P.; Yang, L.; Zhou, J.; Deng, Y. Anthranilic acid from Ralstonia solanacearum plays dual roles in intraspecies signalling and inter-kingdom communication. *ISME J.* **2020**, *14*, 2248–2260. [CrossRef] [PubMed]
85. Darlington, L.G.; Forrest, C.M.; Mackay, G.M.; Smith, R.A.; Smith, A.J.; Stoy, N.; Stone, T.W. On the Biological Importance of the 3-hydroxyanthranilic Acid:Anthranilic Acid Ratio. *Int. J. Tryptophan Res.* **2010**, *3*, 51–59. [CrossRef]
86. Prasher, P.; Sharma, M. Medicinal chemistry of anthranilic acid derivatives: A mini review. *Drug Dev. Res.* **2021**, *82*, 945–958. [CrossRef] [PubMed]
87. Nasr, T.; Aboshanab, A.M.; Abouzid, K.A.M.; Zaghary, W. Hands-on Synthetic Approaches and Biological Activities of Anthranilic Acid Derivatives: A mini-review. *Egypt. J. Chem.* **2023**, *66*, 329–343. [CrossRef]
88. Marinova, P.; Hristov, M. Synthesis and Biological Activity of Novel Complexes with Anthranilic Acid and Its Analogues. *Appl. Sci.* **2023**, *13*, 9426. [CrossRef]
89. Korent, A.; Soderžnik, K.Z.; Šturm, S.; Rožman, K.Z. A Correlative Study of Polyaniline Electropolymerization and its Electrochromic Behavior. *J. Electrochem. Soc.* **2020**, *167*, 106504. [CrossRef]
90. Deng, H.; Van Berkel, G.J. Electrochemical Polymerization of Aniline Investigated Using On-Line Electrochemistry/Electrospray Mass Spectrometry. *Anal. Chem.* **1999**, *71*, 4284–4293. [CrossRef]
91. Huner, K.; Sarac, B.; Yüce, E.; Rezvan, A.; Micusik, M.; Omastova, M.; Eckert, J.; Sarac, A.S. Iron oxide–poly(m-anthranilic acid)–poly(ε-caprolactone) electrospun composite nanofibers: Fabrication and properties. *Mol. Syst. Des. Eng.* **2023**, *8*, 394. [CrossRef]
92. Sarvari, R.; Massoumi, B.; Jaymand, M.; Beygi-Khosrowshahi, Y.; Abdollahi, M. Novel three-dimensional, conducting, biocompatible, porous, and elastic polyaniline based scaffolds for regenerative therapies. *RSC Adv.* **2016**, *6*, 19437. [CrossRef]
93. Li, G.; Zhang, C.; Li, Y.; Peng, H.; Chen, K. Rapid polymerization initiated by redox initiator for the synthesis of polyaniline nanofibers. *Polymer* **2010**, *51*, 1934–1939. [CrossRef]
94. MacDiarmid, A.G. Polyaniline and polypyrrole: Where are we headed? *Synth. Met.* **1997**, *84*, 27–34. [CrossRef]
95. Gupta, B.; Prakash, R. Synthesis of functionalized conducting polymer "polyanthranilic acid" using various oxidizing agents and formation of composites with PVC. *Polym. Adv. Technol.* **2011**, *22*, 1982–1988. [CrossRef]
96. Khalil, A.A.; Shaaban, A.F.; Azab, M.M.; Mahmoud, A.A.; Metwally, A.M. Synthesis, characterization and morphology of polyanthranilic acid micro- and nanostructures. *J. Polym. Res.* **2013**, *20*, 142. [CrossRef]
97. Ulaeto, S.B.; Ravi, R.P.; Udoh, I.I.; Mathew, G.M.; Rajan, T.P.D. Polymer-Based Coating for Steel Protection, Highlighting Metal–Organic Framework as Functional Actives: A Review. *Corros. Mater. Degrad.* **2023**, *4*, 284–316. [CrossRef]
98. Tian, Z.; Yu, H.; Wang, L.; Saleem, M.; Ren, F.; Ren, P.; Chen, Y.; Sun, R.; Sun, Y.; Huang, L. Recent progress in the preparation of polyaniline nanostructures and their applications in anticorrosive coatings. *RSC Adv.* **2014**, *4*, 28195–28208. [CrossRef]
99. Fuseini, M.; Zaghloul, M.M.Y.; Elkady, M.F.; El-Shazly, A.H. Evaluation of synthesized polyaniline nanofibres as corrosion protection film coating on copper substrate by electrophoretic deposition. *J. Mater. Sci.* **2022**, *57*, 6085–6101. [CrossRef]
100. Nguyen, V.A.; Kuss, C. Review—Conducting Polymer-Based Binders for Lithium-Ion Batteries and Beyond. *J. Electrochem. Soc.* **2020**, *167*, 065501. [CrossRef]
101. Maghraby, Y.R.; El-Shabasy, R.M.; Ibrahim, A.H.; El-Said Azzazy, H.M. Enzyme Immobilization Technologies and Industrial Applications. *ACS Omega* **2023**, *8*, 5184–5196. [CrossRef] [PubMed]
102. Shen, H.; Wang, Q.; Chen, Z.; Rong, C.; Chao, D. Application and Development of Silicon Anode Binders for Lithium-Ion Batteries. *Materials* **2023**, *16*, 4266. [CrossRef] [PubMed]
103. Toki, G.F.I.; Hossain, M.K.; Rehman, W.U.; Manj, R.Z.A.; Wang, L.; Yang, J. Recent progress and challenges in silicon-based anode materials for lithium-ion batteries. *Ind. Chem. Mater.* **2024**, *2*, 226–269. [CrossRef]
104. Wang, F.; Chen, G.; Zhang, N.; Liu, X.; Ma, R. Engineering of carbon and other protective coating layers for stabilizing silicon anode materials. *Carbon. Energy* **2019**, *1*, 219–245. [CrossRef]
105. Feng, Y.; Xu, Y.; Liu, S.; Su, D.Z.; Chen, G.; Liu, J.; Li, G. Recent advances in enzyme immobilization based on novel porous framework materials and its applications in biosensing. *Coord. Chem. Rev.* **2022**, *459*, 214414. [CrossRef]
106. Fopase, R.; Paramasivam, S.; Kale, P.; Paramasivan, B. Strategies, challenges and opportunities of enzyme immobilization on porous silicon for biosensing applications. *J. Environ. Chem. Eng.* **2020**, *8*, 104266. [CrossRef]