The Alphabet of Nanostructured Polypyrrole

Subjects: Polymer Science

Contributor: Sylwia Golba , Jan Loskot

Polypyrrole is a significantly useful material derived from an inconspicuous pyrrole ring. The available synthetic procedures allow for the precise sculpturing of both the chemical composition and morphology of the forming polymer. Multiple variations shall be taken into consideration to take advantage of the synergy effect coming from the sophisticated nanostructuring of the material at the stage of choosing the polymer procedure (proper solvent, doping ion, substrate choice), during the polymerization (conditions like temperature, stirring, enhanced impulses, like ultrasounds) or at the post-synthetic functionalization stage.

polypyrrole nano-organization morphology drug delivery neural electrodes

1. Introduction

There is a famous conducting polymers (CPs) triad that includes polythiophene, polyaniline, and polypyrrole (PPy). Among them, it is PPy that is highly attractive due to its wide range of applications. Its utilization spans outer-coating layers [1][2], sensors [3], drug-delivery sponges [4], charge storage in batteries [5], photothermal therapy in cancer [6], and electrodialysis [7]. The form of usage depends on the properties of the polymer and can be tailored to a large extent. It can be deposited as a protective thin layer for oxidizable metals [1] or as a powder [8] in chemical synthesis.

Electroactive conductive polymers can be oxidized (or reduced) by changing the electronic structure of the polymer backbone. The process is accompanied by a charge compensation event as a counterion moves into or out of a layer, forming a kind of ion-enriched sponge [9], an ion gate in the form of a membrane [10], or a hydrogel [11]. Polypyrrole is positively charged in an oxidized state and is neutral and hydrophobic in a reduced state. The ion movement possibility was utilized for the construction of potential controlled drug-delivery systems [4][12]. Many synthetic procedures with multiple ions were studied in this field, with salicylates [13], dexamethasone [14], or chlorpromazine [15] as examples. Drug release kinetics and efficiency served to relate the interconnections between synthetic procedure parameters and system work efficiency. The key parameters affecting the release kinetics of mostly ionic species were studied with the use of various analytical tools like fluorescence spectrometry [16], quartz crystal microbalance (QCMB) [15], or high-performance liquid chromatography (HPLC) [17]. Besides its electroactivity, PPy exhibits also antibacterial properties [8][18]. The tunable photophysical properties of PPy like photothermal conversion ability or Fenton catalysis ability allow for another emerging application, which is cancer therapy for tumor ablation and immune activation [19][20]. Photothermal therapy (PTT) utilizes heat generated locally by light-absorbing agents under near-infrared (NIR) laser radiation [20][21]. The photothermal potential of PPy particles for cancer treatment using NIR absorption was first demonstrated by Yang for material synthesized by aqueous-phase polymerization [22], where tumor growth was inhibited for the NIR laser irradiation (0.5 W/cm^2) of the PPy treated samples. The bioinert surface of polypyrrole makes it a prospective contrast agent for photoacoustic imaging [23] studied with the different steric stabilizers of the dispersion polymerization like dextran (Dex) [24]. Smart scaffolds aimed at improving the functionality of the cardiac tissue were proposed by blending PPy into silk fibroin (SF) [25].

The coating ability of PPy makes it a suitable material for the modification of various substrates, imparting multiple functionalizations with prevailing “anti”- or “super”-type characteristics, like antioxidant [26][27], antibacterial [28][29][30], antifungal [31], superhydrophobic [32], anticorrosive [33], antistatic [34], anti-biofilm [35], anticancer [36], antitumor [37] properties. The application of intrinsically conducting polymers as new coatings presents the possibility of the re-passivation of pinholes in organic coatings [38] because of their inherent redox activity. They are also the base for the formation of smart self-healing coatings [2][39]. Protective polymeric film application for industrial substrates was thoroughly discussed by Saviour A. Umoren [40], mainly in terms of anticorrosion coatings and corrosion inhibitors, pointing to the challenges faced by the extended use of polymers for metal protection.

2. Deposition of Electroactive Polypyrrole

Polypyrrole can be synthesized with various approaches using two main methods, namely chemical oxidative polymerization and electrochemical polymerization. For both methods, the template-based approach can be used to the induce nanostructural organization of the polymer [41], while one has to be careful not to destroy the previously formed organization at the template removal stage [42][43]. Also, other less common methods have been proposed, like radiolytic [44], sono-enhanced [45], or cell-assisted enzymatic processes [46].

Material prepared by the oxidation of the monomer with chemical oxidants (usually $FeCl_3$ (either aqueous or anhydrous) [47], $K_3Fe(CN)_6$ [48], H_2O_2 [49], or an enzyme-mediated system [50]) is black powder. Both the yield and conductivity of the final PPy powder depend on parameters like solvent polarity, type of oxidant, pyrrole/oxidant molar ratio, duration, and temperature of the reaction [51]. Covering other materials with PPy coatings from chemically derived powder is problematic. The idea to overcome this obstacle was realized by polymer deposition from the gas phase [52] or by the preparation of composites with poly(N-vinylcarbazole) [53], poly(ethylene oxide) [54], polyvinyl chloride [55], poly(vinyl alcohol) (PVA), poly(vinyl acetate) (PVAc) [56], polyurethane [57], carbon black [58] or proteins like silk [59]. Other forms of materials containing PPy are also available, like substituted polymers, self-doped polymers, polymer/macroion materials, and hybrid materials (where the macroion is inorganic, polymeric, or of an organic blend) [60].

The electrosynthesis of PPy is initiated electrochemically, with the anodic oxidation of monomer leading to subsequent polymer formation. Concurrently, oxidation (doping) of the previously formed polymer occurs, as evidenced by the amount of consumed charge (2.07 to 2.60 F per mole of monomer with 2 F mol devoted to monomer oxidation) [51]. The electropolymerization mechanism has been thoroughly investigated [51][61][62] and involves several stages. The general process starts with monomer oxidation, followed by the coupling reaction, accompanied by the incorporation of the counterion. A charged polymer attracts anions to balance the charge. In the polymer formation process, both anions and electrons move through the film [62]. In the subsequent reduction, electroneutrality is restored by expulsion of the anions or by the incorporation of cations from the electrolyte solution. Upon the application of a positive potential, the neutral film is oxidized, and the anions are inhaled or cations are ejected. The redox activity of a polymer is governed by the electron transfer reaction and mass transport process [62]. The activity brings about serious structural changes manifested by conformation changes, swelling, shrinking, compaction, or relaxation [60]. For standard CP, de-doping is accompanied by the expulsion of anions along with polymer contraction [63]. In the case of anion immobility, movable cations penetrate the polymer to neutralize charge with observed expansion. In the work of Wallace, electrochemical atomic force microscopy (EC-AFM) was used to trace the dynamic actuation of polypyrrole films doped with polystyrene sulfonate [63]. The observation of actuation height displacement gave insight into factors limiting charge balancing processes, either of diffusion or current nature.

Electrosynthesis is a multi-step process where the yield and quality of the product are determined by factors like pH, electrode nature (e.g., material and shape), temperature, kind and concentration of monomer/counterion, applied procedure and potential value, solvent nucleophilicity, stirring conditions, and the presence/absence of gas bubble [61]. It is a sophisticated art to optimize and control all parameters in a single experiment. As the oxidation potential of pyrrole is lower (0.7–0.8 V) than that of other heterocyclic monomers and water, it is convenient to use it in the process [62][64][65]. At the beginning of polymer deposition, the reaction proceeds in the solution where oligomers are formed. As the chain length increases, they lose solubility, and the nucleation of PPy on the electrode surface occurs [51].

The electrochemical method is advantageous for many reasons, including the straightforward formation of the electroactive film attached to the electrode surface in situ during the polymerization. Moreover, the process has a high yield concerning the consumed charge, which allows for the control of deposited mass and film thickness [42]. The working electrode for electrosynthesis is dictated by the intended usage and is frequently produced with materials stable at an anodic potential like Pt [66], Au [15], ITO-coated glasses (In_2O_3/SnO_2) [67], FTO (fluorine-doped tin oxide) [41]. Also, the syntheses of PPy on stainless steel [68], Fe [69], Cu [70], Ni [71], Ti [72], NiTi [73], Ta [74], glassy carbon [75], graphite [76] or tungsten [77] were proposed. However, electrosynthesis on active metals competes with the metal dissolution possible in the relatively high oxidation potential condition [31]. The method used to overcome this problem is to cover the surface with a protective passive film before electropolymerization to prevent the dissolution of a substrate.

The external signal imposed to invoke oxidation may have different forms; hence, various electropolymerization techniques may be applied, including potentiostatic [78], galvanostatic [79], potentiodynamic [80], or pulsed [81] techniques.

The properties of materials derived chemically and electrochemically are different. As shown by J. Joo [82] for chemically synthesized materials (dodecylbenzene sulfonic acid (DBSA) or naphthalene sulfonic acid (NSA)-doped), the density of states was markedly lower in comparison to electrochemically synthesized ones (PF_6-doped). One dopant molecule was captured per three pyrrole rings in the PPy-DBSA and PPy-PF_6 samples. At the same time, it was an electrosynthesis product that was more branched in the form of side chains or crosslinks (33%) than a chemical one (20%) [82][83]. The authors deduced that for the chemical technique, the use of large-size dopants was a crucial factor for the reduction in side chains or cross-linking. However, such a structure results in two opposite effects increasing solubility, also weakening the interchain interaction that reduces charge transport ability.

3. Polypyrrole Doping and Conduction Path

CPs exhibit the optical and electrical properties of metals with the chemical properties of conventional polymers [84]. The conductivity of these materials comes from loosely bounded electrons in the backbone (as in metals) or from the doping process (as in semiconductors) [85]. For PPy, the conduction mechanism is strongly related to the motion of charge carriers named polarons and bipolarons (biradical cations) along the conjugation framework [61][85]. The oxidation level, manifested by the doping degree of the polymer, usually approaches 0.25–0.32 per pyrrole ring [51], depending on the kind and the charge of the inhaled anion. This means that one anion affiliates to 3–4 pyrrole units, accounting for 30–40% of the weight of the polymer [82]. There are an enormous number of ions utilized for doping PPy, including simple inorganic, monovalent ones like chloride [86]; organic ones like dodecylbenzene sulfonic acid (DBSA) [87] and *p*-toluene sulfonic acid (pTSA) [31]; large organic ones like sodium dodecyl sulfate SDS [80]; polymeric ones like polystyrene sulfonate (PSS^-) [63]; DNA [88]; or polysaccharides like heparin [89]. The type and size of the ion induce a profound effect on the electronic, optical, and biomechanical properties of CPs [90], e.g., polymers prepared with pTS^- were shown to be more stable than PPy doped with ClO_4^-, BF_4^- or NO_3^- [55]. The changes in the electrolyte nature, e.g., passing from a small anion such as ClO_4^- to a large polyanion such as poly(sodium-4-styrene sulfonate) NaPSS leads to the formation of thicker PPy–PSS hollow nanotubules [91].

The relationship between polymerization rate and monomer concentration changes from linear for small doping anions to exponential for large doping anions such as PSS [92]. Large polyelectrolyte ions are firstly adsorbed on the electrode surface, thus retarding the monomer oxidation process. However, once the monomer oxidation is initiated, this process becomes much faster for increased polyelectrolyte concentration. The type of utilized dopant also influences the distribution of charge carriers in polypyrrole thin films, as shown by Pen-Cheng Wang [86] for chloride-, *p*-toluenesulfonate-, and anthraquinone-2-sulfonate-doped materials. The variation of dopant anion manifested in a change in the conductivity of thin films by three orders of magnitude (0.64 S/cm, 7.1 S/cm, and 120 S/cm, respectively) [93].

The anion incorporated into the polymer at the stage of synthesis also influences the thermal stability [61]. It was pointed out in many works that the thermal stability of PPy should be improved, especially in oxidative atmospheres such as air [61]. Additionally, research impact on the enhancement of mechanical properties is urged for prospective applications. The aspect of aging polypyrroles derived by the chemical method was discussed by Mičušík [94], who reported that during the tests, -N-C=O carbonyl groups were formed after oxygen attack, mainly at the α position of the pyrrole unit. SO_4^{2-}- and $S_2O_8^{2-}$-doped materials had shorter conjugation lengths, owing to the interaction of sulfate groups with the polymer chains to create sulfonic functional groups. The use of anionic surfactant (DBSA) as a co-dopant improved the stability in ambient air [94].

Thinking of the technological application of PPy also overoxidation process should be taken into consideration [95][96]. Profound changes in material properties may occur after being exposed to oxidizing conditions or very positive electrode potentials [95]. It was proved that the hydroxyl radicals formed during water oxidation are responsible for PPy oxidative degradation [96]. The changes lead to the irreversible depletion of the electroactivity, also resulting in the decreased diffusion of ionic species. Still, it may be beneficial for some applications such as protection against electrode fouling, provision of permselectivity, action as a host or cover for immobilized reactants, and provision of the material for molecular imprinting [88][95][97].

The reversible variation of volume associated with the electrochemical reduction–oxidation processes was studied by Otero [98]. If a polyelectrolyte or an organic macroanion is incorporated into a CP, then the electrochemical process induces changes in free volume, which is a counterbalance of two effects, namely electrostatic repulsions between immobile macroanions and the exchange of ions and solvent molecules between the polymer and the solution.

The oxidation of polypyrrole depends on crossing the activation energy, which includes two components—chemical activation energy and the energy connected to the relaxation of the polymeric structure induced by the entrance of counterions. The value of the second component relates to changes in the film’s molecular structure during the process and film thickness [99].

4. Morphology of Polypyrroles

The morphology of material pictured by the SEM or optical images is the result of the events that occur at the lower stages of organization. The mutual inter- and intramolecular interactions silenced or strengthened by the chemical composition of the reaction environment, synthetic procedure, or post-synthetic modification lead to the formation of specific arrangements. The surface morphology alone cannot sufficiently characterize the whole polymer layer structure, but it is the outfit of the event that takes place within the macrochains and between participants of the synthetic process. The knowledge provided by studies of surface morphology and its origin can provide suitable methods for the synthesis of films with required properties in reverse engineering mode. For a typical polypyrrole, a usual cauliflower morphology is known. However, through the manipulation of the available factors, it can be significantly altered for materials deposited in the presence of different counterions. When adjusting synthesis duration, the shorter times produced thin films of similar characteristics. The extended time provided thicker films with distinct topography, which proved that counterions influence topography [100].

It is interesting as one-dimensional (1D) nano-structure materials extend the application areas in comparison to bulk ones, which are frequently composed of spherical particles. The 1D morphology of the particles lowers the percolation threshold and increases the specific surface area. This leads to higher electrical conductivity along with improved stability. Such products are usually characterized by uniform morphology, low polydispersity, and a high aspect ratio. It was found that the nanostructured organization depends on the polymerization rate and can be supported by the use of additives like a steric stabilizer (polyvinyl pyrrolidone (PVP)) [101].

Several electrochemical methods for the synthesis of nanostructured PPy were reviewed by Bocchetta [102] along with template-based or template-free polymerization. The role of hard templates (like ZnO nanorods, α-Fe_2O_3 nanowires, silica and silicon-based templates, anodic TiO_2 nanotubes, and colloidal crystals) were elegantly presented. Also, several methods for self-assembly template-free methods (like surfactant micelles, gas bubbles, or azo dyes complexes) were delivered [102]. The main parameters that govern the ability to self-assemble PPy nanofibers in electrodeposition (template-free process) are pH, applied potential, monomer type, and doping ion concentration. Diverse interfaces and morphologies of polymer nanodeposits were formed, and plausible mechanisms of their formation were discussed. The composition of solution and the formation of weak interactions between molecules are the leading forces that impose on the self-alignment ability of PPy [102]. A similar effect was found for cone-shaped PPy deposited on an Au substrate in a concentrated monomer solution (concertation up to 0.6 M) [103].

4.1. The Impact of Morphology on the Bio-Applicability of PPy

4.1.1. N as Neural Applications

Conducting polymers exhibit ionic and electronic conduction and resemble the mechanical and conductive properties of living organisms. This makes them interesting materials for application in the bioelectronic field [104]. They are proposed as coatings of neural and osteogenic implants for signal recording and electrical stimulation. The idea is based on the ability of a material to overtake high-efficiency signal transduction at the interface while staying ion-permeable. Some strategies were proposed for such implants to enhance cell−substrate and cell−cell interactions, providing an artificial matrix resembling ECM (extracellular matrix) behavior in terms of chemical, topographical, and mechanical properties. Histological analyses of tissue surrounding polypyrrole-based implants in rats showed an immune cell response similar to poly(lactic-co-glycolic acid), which is an FDA (Food and Drug Administration)-approved material [105]. For PPy-based sciatic-nerve guidance channels implanted in rats, low inflammatory responses were reported [106]. Substrate roughness and chemical functionalization are useful tools to adjust mimicry strategies on CPs [104]. However, the implants often fail due to bacterial infection [107]. Working on conducting materials in living organisms requires mindfulness as imposed electrical signals induce multiple effects on the cells, like the rearrangement of the cytoskeleton, the depolarization of the plasma membrane, the alternation of protein conformation, or the modulation of membrane ion influx [84].

Effective neural interfaces require materials able to convert neural signals to digital ones. A list of desired material properties was delivered by Krukiewicz covering low electrical impedance accompanied by high cathodic charge storage capacity, high charge injection capacity, and electroactive surface area, with adequate mechanical characteristics [108]. The formation of responsive, durable, and selective implantable bioelectrodes is the aim of many research teams in the field of bioelectronics applications [109][110][111]. Available electrodes are formed with mechanically hard metallic materials that do not fit with biological tissue that is soft, ionically based, wet, and dynamic. Their interaction leads to reactive tissue responses and electrode encapsulation. The low surface area of these electrodes reflecting the planar microscale geometry translates into disadvantages of the application, low signal-to-noise ratio, high impedance, and low charge injection capacity at electrode–tissue interfaces [112]. There are multiple ideas for overcoming these obstacles by optimizing size and shape, choosing substrate material, bioactive coating deposition, or delivering drugs. The performance of devices can be also improved by the organization of PPy at the nano level [102]. Decreased distance to transport ions along the chains converts into enhanced electrical conductivity and the reduction in the impedance at the electrode/electrolyte interface. Through nano-organization, deposited materials induce electrical advantages by increasing the surface area related to nodular morphology, which elevates resistance to the mechanical stress derived from the electrochemical half-reaction. The neural tissue performance is dependent on physical properties imposed by the topography, roughness, or mechanical rigidity of materials [90].

4.1.2. A as Antibacterial and Implantable Applications

The antibacterial behavior of PPy depends on a diversity of structural parameters such as surface area, aggregation level, and additive (e.g., metal nanoparticles) incorporation [8][29]. These properties are related to polymerization solution compositions and conditions; hence, the final material characteristic is a compromise between them [113]. For example, electrochemically deposited PPy with p-toluenesulfonate (TsO^-) dopant is highly conductive [114] but still does not show enhanced antibacterial activity [31].

The real battle takes place locally; hence, the core antibacterial inhibition mechanism is relevant to the interaction between the atoms of the biomaterial and the bacteria. The mechanism relies on an electrostatic interaction between the positive charges located on the polymeric chains and the negative charges located on the membrane cell of the bacteria [3]. The attack on the cell wall of the bacteria by the charged N atom and dopant ions of the polymers is possible. Changes in the preparation procedure impact the parameters modifying its resilience, e.g., by controlling the sizes of PPy nanoparticles. The electrostatic interaction of polymer nanoparticles with bacteria leads to bacterial cell death. The characteristic time-kill of bacteria in contact with the chosen agent proved the superior bactericidal activity of highly soluble PPy with a minimal period of interaction to inhibit the growth of bacteria like *E. coli*, *K. pneumoniae*, and *S. aureus* [8]. The PPy effect on *P. zopfii* cells (saprophyte microorganisms involved in the occurrence of infections) was verified by Ely [115] with an evident decrease in the number of cells after treatments with sublethal doses of PPy, both in planktonic and sessile forms. After the evaluation of the effectiveness in vivo, a formulation could be prepared to treat the animals naturally affected by *Prototheca* spp. [115]. Smart antimicrobial material with dual functionality was prepared by Děkanovský [116] by dosing stretchable polydimethylsiloxane (PDMS) with polypyrrole. The composite was found to be superhydrophobic with self-cleaning ability. The presence of a conductive additive provoked the ability to electrically trigger the release of an immobilized model drug (namely crystal violet). Focusing on morphology, it is visible that the mixing of components markedly increases the surface roughness, forming typical aggregates. The antimicrobial protection tests in the *E. coli* solution showed a lack of bacteria adhesion on the surface, while applying electric field-induced interaction with the bacteria was accompanied by changes in the sample morphology [116]. A duplex coating formed potentiostatically on a magnesium alloy (AZ91D) was studied by López [117][118] in a simulated physiological environment. A dual system composed of a pristine protective layer deposited in molybdate solution and covered with the outer layer of PPy film was electrosynthesized in a solution of sodium salicylate.

A multifunctional polypyrrole/zinc oxide (PPy/ZnO) composite was deposited with the CV method on Mg alloys [119] with perspective applications in the field of orthopedic implant materials. Based on the result of an in-vitro test, improved adhesion and proliferation of cells were confirmed. This was accompanied by significant antibacterial ability against *E. coli* at the level of 96.5 ± 2.6%, with coarse and wrinkled bacteria cells [119]. In the search for the better osseointegration of titanium-based implants, a new lanthanum-substituted hydroxyapatite(HAP)/poly(N-methyl pyrrole) (pNMPy) coating was proposed by Mathi [120].

Nano-functionalized polypyrrole with high surface potential was the subject of the study of Zhou [121]. In the template-free procedure, sulfosalicylic acid (SSA) was used to assist in the ordering of PPy macrochains and to modulate the surface electrical properties of the coating. SSA-doped PPy nanorods were successfully built on a titanium substrate with a diameter of approximately 100 nm, increasing specific surface area markedly. The material was proved as an antibacterial in comparison to irregular PPy/Cl, which was prescribed to two factors—nanorod morphology and high surface potential induced by the dopant [121].

Potentiostatically synthesized polypyrrole deposited by Martinez [122] on Ti-6Al-4V alloy is aimed at dental implant applications. Zn particles were immobilized either during or after the process within the microstructured matrix, with the second method being more effective in terms of antibacterial activity. SEM micrographs of the coatings presented hollow rectangular-sectioned microtubes of polymer deposited in the presence of salicylate ions. The organization event relates to the precipitation of rectangular structures of salicylic acid triggered by the decreased pH, with subsequent polymer deposition at the walls of the formed crystals [123].

The coating of a carbon steel surface with PPy, aimed at improving corrosion resistance along with antimicrobial properties, was proposed by Jaouhari [124]. PPy films synthesized galvanostatically reproduced compact distribution with globular components of sizes in a range of 2 to 10 nm. The structural changes between the films were imposed by a deviation in the polymer growth mechanism. It was proposed that the implosion of the cavitation bubbles on the surface of the electrode produced many nucleation sites. The antibacterial activity quantification proved high activity for PPy-coated steel with silver, accompanied by reduced Fe^{2+} ion release [124]. Polypyrrole films embedded with copper cations were deposited on 316 L stainless steel and tested as a water disinfection system [125]. SEM images of a PPy-Cu-coated electrode revealed PPy microtubes that were not damaged after examination in the lab-scale continuous flow tests system, and they were not adsorbed with the bacteria cells.

The electrosynthesis of polypyrrole on nitinol proposed by Saugo [73] led to materials for which morphology was influenced by the electrolyte (sodium salicylate, NaSal) concentration. For a low concentration of NaSal (0.10 M), the standard globular morphology was obtained, while the increase in concertation (to 0.50 M) changed it into hollow microtubes of rectangular shape. These hollow tubes were utilized for silver immobilization within the PPy matrix, with quantitative dependence on the polymer oxidation degree [73]. The antibacterial activity of the coating was manifested in the test against the Gram-positive *Staphylococcus aureus* and *Staphylococcus epidermidis* bacteria.

4.1.3. D as Drug-Delivery Platforms

Drug-delivery systems constructed on CPs use the polymers' ability to electrical switch between an oxidized and a reduced state, accompanied by the uptake or expulsion of charged molecules from the bulk of the polymer [12]. Drug loading can be realized in several ways depending on the type of the molecule: a one-step immobilization procedure for small anionic compounds, such as dopants; a three-step method where the synthesis and drug loading are separated; and a modified three-step method for cationic drugs.

The release of such substances from ICP matrices is governed by electrostatic forces [126] accompanied by expansion and contraction movements induced by the electro-chemo-mechanical response [98]. These two phenomena take place simultaneously and their interplay determines system-releasing efficiency. The polymer nanostructure also impacts the rate-limiting mechanisms of the ion diffusion and exchange process [127]. Cui investigated the impact of the morphology of substrate electrodes on electrically controlled drug release from PPy [128]. Fluorescein acted as a model drug, playing the role of the doping ion, while gold electrodes were covered with platinum to elevate the surface roughness of the substrate. All measured parameters, like the range of electrical stimulation of fluorescein release from the electrode, release per charge accumulation used during electropolymerization, and release per charge injected during electrical stimulation, confirmed an increase in the release of the drug from the material of higher roughness [128]. The drug loading capacity in electrically stimulated DDS is relatively low and there are different concepts concerning how to increase it.

Drug-delivery systems composed of a modified polypyrrole film with diminished ion exchange of the stored compound were proposed by Arbabian [129]. A millimeter-sized implant electronically controlled the drug release and was powered ultrasonically. Fluorescein-loaded polypyrrole nanoparticles were synthesized with a micelle-templated method and subsequently aerosol spray-coated onto the modified screen-printed electrode. The morphological analysis showed the high surface area of the resulting nanoparticulate film with pore sizes that enhanced drug loading and facilitated the release act [129].

The polymerization of Py to nanostructural forms can be guided by a template method that is either soft or hard [63]. In electrochemical polymerization, the hard template is conductive or covered with a conductive surface. In the process, polymers with defined micro- or nanostructures are obtained. In the subsequent removal step, the template can be dissolved, leaving an imprint of the material. Abidian utilized such a procedure to fabricate monodispersed conducting polymer microcups [130].

4.1.4. S as Sensors and Sorbents

The use of conjugated polymers for sensing applications is beneficial, as the intrinsic conductivity of matrices provides a tool for fabricating highly sensitive chemoresistive sensors. Numerous studies of sensors have been reported [131][132][133][134], with polypyrrole being one of the most promising in the field because of its stability and biocompatibility. Multiple available electrochemical deposition techniques are also an advantage. Cyclic voltammetry at different scan rates (5–50 mV/s) was utilized for the synthesis of polypyrrole on a gold electrode surface [135]. Deposited material was used for the electrochemical reduction in the simulant of nerve agents, namely dimethyl methyl phosphonate (DMMP), in an aqueous environment. SEM image analysis pointed to correlation of scan rate with surface morphology, showing globular, growing bud, hook, or rod structures. A decreased value of R_{et} (the electron transfer resistance) was reported for electrodes modified at 10 mV/s manifested in an extended surface area that enhanced electron transfer in the thin film of PPy [135]. The functionality of a dual-template molecularly imprinted polymer (DMIP) as a sensing layer to alpha-fetoprotein (AFP) and a carcinoembryonic antigen (CEA) as a lung cancer biomarker was verified by Bagheri [41]. PPy deposited on a fluorine-doped tin oxide (FTO) electrode served as an artificial antibody-like system. The characteristic morphology was a non-grown globular structure with an average diameter of particles of 1100 nm. The presence of a template molecule (methylene orange, MO) induced organization, with a surface morphology of periodically dispersed hollow rectangular nanotubes. In the case of PPy-MO DMIP, the coating has a rougher structure dictated by the presence of biomarkers at the stage of electropolymerization. The addition of AFP (or CEA) influenced template formation due to the interaction with MO, e.g., by hydrogen bonding, and varied the polymeric structure of the imprinted layer [41]. Impedimetric detection served as a tool for rebinding the template detected with the charge transfer resistance, which increased as the concentration of AFP and CEA increased.

An elegant immunosensor for the detection of anti-transglutaminase antibodies was constructed utilizing an overoxidized polypyrrole matrix [136]. A transglutaminase (tTG)-specific antibody represents a specific biological marker for coeliac disease. In the process, the transglutaminase antigen was deposited on a polymer, and gold nanoparticles covered a glassy carbon electrode. With the use of the EIS, the linear relationship between charge transfer resistance and analyte concentration was established. The SEM images of the AuNP and oPPy composite showed the transformation of material in the course of the overoxidation process—from a flake-like C_4^--doped system to a typical “cauliflower-like” structure. The good surface coverage of the film surface with AuNP was noted [136]. The application of the sensor was verified using a calibration curve for known antibody concentrations.

A nanohybrid film of carboxylated polypyrrole and amine nanoclay was prepared as an immunosensor for the label-free detection of the human cardiac troponin T (cTnT) [137]. The nanohybrid film was formed in situ on the surface of the glassy carbon electrode, followed by the covalent immobilization of anti-troponin T antibodies using glutaraldehyde. The morphology of the film showed agglomerates of different two-dimensional laminar shapes. An interesting review focusing on the use of polypyrrole-based electrochemical biosensors for the diagnosis of colorectal cancer was provided by Wang [138] pointing to opportunities and challenges related to the use of PPy-based sensors for diagnosing colorectal cancer (CRC).

The electrosorption/electrodesorption process was utilized for the detection of salicylic acid (SA) with the aid of electrochemically controlled solid-phase extraction (EC-SPME) [139]. Nitrate-doped polypyrrole was a sorbent for the extraction of SA in plasma and urine samples. A rod-shaped stainless-steel electrode was covered with the vertically grown nanosheets deposited with the CV method. The morphology of the nanostructure PPy/nitrate sorbent revealed the presence of nano-sheets with a diameter of 14 nm, pointing toward a more porous, three-dimensional structure in comparison to the SDBS-doped system. It was validated to be more efficient for the electrosorption of chosen analytes [139].

CPs are regarded as promising materials for monitoring environmental pollution, as CP-covered electrodes have been tested for the selective recognition of heavy metal ions in water [140]. The efficiency of an electrosensing electrode material relies on several parameters like the type of dopant; the modification of the polymer backbone, e.g., by chelating groups; or the preparation of an ion-imprinted matrix. The nanostructuration of sorbent material improved the sensitivity of sensors for quantitative and rapid analyses. A polypyrrole/zeolite nanocomposite was proposed as a nanoadsorbent for reactive dye, namely reactive blue (RB) and reactive red (RR), removal from synthetic solution [141]. PPy/Ze nanocomposite particles were agglomerated with a spherical shape with an average size of 40–80 nm that was not changed after the adsorption of dyes.

4.2. The Impact of Morphology on the Technological Applicability of PPy

4.2.1. P as Corrosion Protection

Corrosion is a continuous obstacle that occurs when metallic substrates are in use. Different materials and approaches were proposed to decrease its impact as well as improve anticorrosion properties. For CP-coated substrates, several protection mechanisms were described, namely anodic passivation, cathodic protection, barrier protection, and a controlled inhibitor release model. Enhanced anticorrosive characteristics were shown for coatings electrodeposited from a solution of pyrrole and oxalic acid on an iron surface [142]. The acid additive provoked the growth of a protective layer composed of iron oxalate, preventing the anodic dissolution of substrate at the applied potentials. The protective properties of PPy-based coatings can be improved by the application of chosen electrodeposition parameters, including the type of doping anion and the construction of a multi-component or multilayer system [80]. For PPy films deposited from sodium salicylate solution synthesized on Ti-6Al-4V alloy potentiostatically [122], Zn was immobilized with two methods in the polymer to both prevent corrosion and deplete microbial growth. SEM micrographs showed the presence of hollow rectangular-sectioned microtubes for PPy deposited in salicylate solution, while the addition of Zn^{2+} ions distorted this shape to some extent, with deposits of zinc salicylate on the top. Both unmodified and modified films delivered corrosion protection by suppressing the active dissolution process in artificial saliva [122]. Similar anodic protection behavior was reported for PPy electrosynthesised on a nickel substrate [82]. Moreover, the adherence of the films markedly increased in this study. The electropolymerization of pyrrole in aqueous solutions of salicylate (0.5 M) was reported by Saidman [143]. The coating morphology presented hollow rectangular-sectioned microtubes. The bilayer system composed of differently doped PPy (underlayer doped with molybdate and nitrate and top layer doped with salicylate) was constructed to test anticorrosive properties. The inner and the outer layers were electrosynthesised at 0.8 V for 180 and 600 s, respectively. It was shown that bilayers were capable of protecting the substrate (316 L SS steel) against uniform and pitting corrosion during prolonged exposure [143]. Mild steel (MS) was covered with homopolymer and bilayer coatings composed of poly(N-methylaniline) (PNMA) and polypyrrole–dodecylsulfate (PPy-DS) using the potentiodynamic method [144]. Th surface morphology of homopolymer and bilayer coatings revealed by SEM images provided a cauliflower-like structure for PPy-DS synthesized in a narrow potential range

(0.3–0.9 V vs. Ag/AgCl), while for the extended range (0.3–1.0 V vs. Ag/AgCl), the fiber-shaped fringes were visible. The PNMA/PPy-DS bilayer was found as the most corrosion-resistant at all immersion times (tested up to 240 h) [144]. The highly anticorrosive behavior and long-term stability of the dodecylsulfate-doped PPy system were confirmed by Syugaev [80].

4.2.2. M as Mechanical Aspects

Π-conjugated polymers combine electronic functionality with mechanical robustness. The materials were tested for their stretchability and flexibility [145], which are required for application in fields like wearable health monitors [146], stretchable electrochemical sensors for cell and tissue detection [147], neurological recording [148], or soft electronics [149]. In [150], the authors analyzed the stress-strain data from pull tests on conjugated polymers to explore the molecular and microstructural parameters that influence mechanical properties. Studies of mechanical properties, namely reduced elastic modulus, indentation hardness, and creep, were reported by Başman [151] for PPy on a Pt working electrode. Data derived from the depth-sensing indentation (DSI) technique showed that a rise in the concentration of support electrolytes reduced both elastic modulus and indentation hardness values. This was correlated with an increase in the free volume accompanying higher doping levels. Additionally, it also resulted in the enhanced creep of the samples [151].

4.2.3. B as Bubbles and Nanoporous Structures

It is possible to form empty nanostructured containers; this is realized by the gas-assisted technique. In the first stage, gas bubbles are inhaled into micelles and adsorbed on the surface of the substrate. In the subsequent step, these structures play the role of a template for PPy deposition [152], which takes the shape of spheres, bowls, and cups. The technique is free from the template removal stage, in opposition to aromatic surfactants like β-naphthalene sulfonic acid (NSA) [153] and poly(styrene sulfonic acid) (PSSA) [154] that are most frequently used. The arrangement forces are mainly dictated by synthetic conditions like vertex potential, the surfactant's concentration, the number of cyclic scans, and solution pH.

Turco provided interesting templates for the synthetic path of PPy nanowires [155] using non-static solution surface electropolymerization. A pivotal role in the deposition on an indium tin oxide-coated PET working electrode was prescribed for the oxidation of pyrrole along with oxygen nanobubble formation. The morphology of the layer was governed by synthetic parameters like flow rate, pH of the electrolyte solution, and time of process. Nanowires with a diameter in the range of 40–300 nm were obtained, with a larger electroactive area of the sample prepared at acidic (pH 6.8) conditions [155]. Picturesque structures were obtained by the use of a gas bubbles-based procedure in the work of Guittard [156], based on the application of thienothiophene derivatives.

Spontaneous nanostructuration was enabled by the oxidation of water followed by the production in hydroxyl radicals and nanobubbles of oxygen. Moreover, the authors proved that the nanobubbles shield the PPy film against the action of the hydroxyl radicals, which react with the polypyrrole film, leading to overoxidation [71][95].

Well-shaped nanostructures were provided in the study of McCarthy [157], where electrodeposition was performed on a glassy carbon rod substrate from an emulsion of pyrrole and its N-functionalized derivative, namely N-(2-cyanoethyl)-pyrrole. The emulsion was prepared by two sonication procedures that resulted in various microstructure formations. The polymer was shaped as aligned open- and closed-pore microtubes, where adsorbed toluene droplets played the role of soft templates supporting polymer growth. The rate of polymer propagation was controlled by the chemical composition of the electrolyte solution, with the ClO_4^- and $H_2PO_4^-$ doping ion concentration being the most appropriate factor [157]. Polypyrrole-coated pickering-type droplets were studied as light-responsive carriers of oily material [158], leading to the light-driven remote motion control of the droplets.

A porous diblock copolymer template, namely a copolymer of styrene and methyl methacrylate (PS-b-PMMA), was utilized in a procedure aimed at the deposition of high-density polypyrrole nanorods on an indium-tin-oxide (ITO)-coated glass electrode [159]. The nanorods were characterized with distinctly higher conductivity in comparison to thin PPy films, which reflected their high degree of chain orientation coming from the synthetic stage, where the growing chains were confined into nanosized cylindrical cavities. When the pore sizes of the templates were more than 50 nm, the nanotubes were formed, while for smaller diameters (<25 nm), nanorods were constructed [159]. The confinement effect in the environmentally friendly synthesis of PPy within advanced polymeric templates was traced by Malardier-Jugroot [160]. Two polymeric templates with different functional groups were used, namely SMA (poly(styrene-alt-maleic anhydride)) and IMA (isobutylene-alt-maleic anhydride)). In the water environment, SMA produced amphiphilic nanotubes with hydrophilic shells and hydrophobic cavities, while IMA produced amphiphilic lamellae sheets with a hydrophilic outer layer and a hydrophobic interior. The chemistry of the templates did not markedly influence the reaction, while the confinement effect was proven to be crucial for the reaction (in block copolymer PS-b-PAA templates, with diameters of 40 to 70 nm, the polymerization did not occur) [160]. Polycarbonate particle track-etched membranes with different pore sizes were used for PPy electrodeposition by Demoustier-Champagnen [90][161].

4.2.4. C as Carbon-Based Materials

In many cases, the good properties of polypyrrole can be even better when a proper other ingredient is introduced to prepare a multi-component system. This seems to be true for the “marriage” of polypyrrole and carbon-based materials, where attempts to provide new materials are highly successful and promising. Different carbon-based substrates (vitreous carbon and Au (111)) as well as various experimental conditions (dynamic vs. static potential protocols) and halogen dopants (I^- and F^-) were tested in the work of Batina [162]. The morphological study revealed that the conditions induced ring (doughnuts) and microcontainer formation. The microstructure formation was contingent on the occurrence of the overoxidation of PPy [162]. The polypyrrole morphology showed significant influence on the BET surface in the studies of Mosch [163], where the porosity and surface measurements revealed the increase in average pore size for composites in comparison to pure carbons (either CB or MWCNT). The highest electrochemical area and mesoporous structure belonged to composite samples, which were also characterized by increased capacitance. It revealed the beneficial aspect of the deposition of polymers on the carbon substrate [163]. The electrochemical capacitance of composite coatings composed of PPy and carbon nanotubes (CNTs) was also investigated in supercapacitor application by Bara [164]. PPy deposited on CNTs on a Ni catalyst layer deposited on a Si/SiO_2 substrate showed uniform coverage with high capacitance in an acid electrolyte [164].

4.2.5. E as Energy Conversion Systems (Solar, Photothermal and Energy Storage Applications)

Conventional energy sources are limited in nature, so other solutions are sought and studied, including marine, nuclear, solar, bio, and wind resources. Solar energy is transmitted with solar thermal technology, photovoltaic energy conversion, and solar hydrogen gas production technology [165]. There are many technologies to convert solar energy; photovoltaics (PVs) is one of the cleanest to choose. Conjugated polymers are used for the fabrication of photovoltaic devices, namely electrochemical and dye-sensitized solar cell (DSSC) devices [166]. The overall efficiency of bulk heterojunction (BHJ) architecture photovoltaic cells depends to a large extent on the nanomorphology of the photoactive layer. It can be tuned by processing parameters like the choice of solvent(s) in the spin-casting method, thermal and solvent annealing, solvent additive, and blend composition [166]. Molecularly imprinted polypyrrole was proposed as counter-electrode material for dye-sensitized solar cells (DSSCs) by Sangiorgi [167]. Moreover, 2-aminoacetic acid (glycine) and L-2-aminopropionic acid (L-alanine) were used as template molecules at the imprinting stage. Gel-state DSSCs based on MIP-PPy CE with glycine were characterized by a 20% increase in the power conversion efficiency along with a 50% reduction in the charge transfer resistance, in comparison to the cells based on NIP-PPy. In terms of the morphology of MIP and NIP PPy electropolymerized on the FTO surface for glycine coating, they showed globular-shaped particles with circular nano-aggregates smaller than the ones found for NIP-PPy. At the same time, for MIP with L-alanine, the presence of small aggregates with needle-like shapes was visible, forming more homogenous film. The differences were prescribed to various molecular surface areas of the two template molecules [167]. Carbon fabric (CF) coated with polypyrrole was used as a flexible counter electrode in DSSC [168]. It showed a homogenous structure along with proper electron/hole charge transfer. The power conversion efficiency (PCE) of the constructed DSSC reached 3.86%. The application of polyoxometalate (POMs: $H_3PW_{12}O_{40}$) led to (PW12)-doped polypyrrole (PW12-PPy) hybrid film tested as an efficient counter electrode in a DSSC [169]. POMS exhibit multi-electronic reversible reactions and good electrochemical catalytic activity, resulting from transition metal oxide components. The average power conversion efficiency of the DSSC illuminated with solar radiation (PCE, 6.19%) was comparable with ordinary Pt-cathode devices. SEM images of the PW12-PPy showed a sphere-like structure with a large specific surface area [169].

5. Conclusions

Polypyrrole is a significantly useful material derived from an inconspicuous pyrrole ring. The available synthetic procedures allow for the precise sculpturing of both the chemical composition and morphology of the forming polymer. Multiple variations shall be taken into consideration to take advantage of the synergy effect coming from the sophisticated nanostructuring of the material at the stage of choosing the polymer procedure (proper solvent, doping ion, substrate choice), during the polymerization (conditions like temperature, stirring, enhanced impulses, like ultrasounds) or at the post-synthetic functionalization stage. The scope of possibilities is greater for composite preparation where a multiphase system is produced. The scientist is supposed to be a designer who uses the right bricks, at the right time, with the right sequence, to obtain advanced materials with high utility. Usually, it is an application field that imposes the required properties and guides us to deliver, e.g., either a highly porous substrate for neural scaffolds or a homogeneous, compact coating for corrosion protection. As we have gained knowledge of the relation between the synthetic path and morphological properties, it is possible to use it in the reverse technology and tailor future materials.

References

1. Kahvazi Zadeh, M.; Yeganeh, M.; Tavakoli Shoushtari, M.; Esmaeilkhanian, A. Corrosion performance of polypyrrole-coated metals: A review of perspectives and recent advances. Synt. Met. 2021, 274, 116723.
2. Yin, Y.; Prabhakar, M.; Ebbinghaus, P.; da Silva, C.; Rohwerder, M. Neutral inhibitor molecules entrapped into polypyrrole network for corrosion protection. Chem. Eng. J. 2022, 440, 135739–135753.
3. El Guerraf, A.; Ben Jadi, S.; Karadas Bakirhan, N.; Eylul Kiymaci, M.; Bazzaoui, M.; Aysil Ozkan, S.; Arbi Bazzaoui, E. Antibacterial activity and volatile organic compounds sensing property of polypyrrole-coated cellulosic paper for food packaging purpose. Polym Bull. 2022, 79, 11543–11566.
4. Krukiewicz, K.; Gniazdowska, B.; Jarosz, T.; Herman, A.P.; Boncel, S.; Turczyn, R. Effect of immobilization and release of ciprofloxacin and quercetin on electrochemical properties of poly(3,4-ethylenedioxypyrrole) matrix. Synt. Met. 2019, 249, 52–62.
5. Chen, Y.; Kang, G.; Xu, H.; Kang, L. PPy doped with different metal sulphate as electrode materials for supercapacitors. Russ. J. Electrochem. 2017, 53, 359–365.
6. Ma, Y.; Zhou, J.; Miao, Z.; Qian, H.; Zha, Z. dl-Menthol Loaded Polypyrrole Nanoparticles as a Controlled Diclofenac Delivery Platform for Sensitizing Cancer Cells to Photothermal Therapy. ACS Appl. Bio. Mater. 2019, 2, 848–855.
7. Ashu Tufa, R.; Piallat, T.; Hnát, J.; Fontananova, E.; Paidar, M.; Chanda, D.; Curcio, E.; di Profio, G.; Bouzek, K. Salinity gradient power reverse electrodialysis: Cation exchange membrane design based on polypyrrole-chitosan composites for enhanced monovalent selectivity. Chem. Eng. J. 2020, 380, 122461.
8. da Silva, F.A.G., Jr.; Queiroz, J.C.; Macedo, E.R.; Fernandes, A.W.C.; Freire, N.B.; da Costa, M.M.; de Oliveira, H.P. Antibacterial behavior of polypyrrole: The influence of morphology and additives incorporation. Mater. Sci. Eng. C 2016, 62, 317–322.

9. Luo, X.; Tracy Cui, X. Sponge-like nanostructured conducting polymers for electrically controlled drug release. Electrochem. Commun. 2009, 11, 1956–1959.
10. Tan, X.; Hu, C.; Zhu, Z.; Liu, H.; Qu, J. Electrically Pore-Size-Tunable Polypyrrole Membrane for Antifouling and Selective Separation. Adv. Funct. Mater. 2019, 29, 1903081.
11. Riaz, U.; Singh, N.; Rashnas Srambikal, F.; Fatima, S. A review on synthesis and applications of polyaniline and polypyrrole hydrogels. Polym. Bull. 2022, 80, 1085–1116.
12. Tandon, B.; Magaz, A.; Balint, R.; Blaker, J.J.; Cartmell, S.H. Electroactive biomaterials: Vehicles for controlled delivery of therapeutic agents for drug delivery and tissue regeneration. Adv. Drug Deliv. Rev. 2018, 129, 148–168.
13. Liu, J.; Liu, Z.; Li, X.; Zhu, L.; Xu, G.; Chen, Z.; Cheng, C.; Lu, Y.; Liu, Q. Wireless, battery-free and wearable device for electrically controlled drug delivery: Sodium salicylate released from bilayer polypyrrole by near-field communication on smartphone. Biomed. Microdev. 2020, 22, 53–63.
14. Ashfaq Ali Shah, S.; Firlak, M.; Ryan Berrow, S.; Ross Halcovitch, N.; Baldock, S.J.; Muhammad Yousafzai, B.; Hathout, R.M.; Hardy, J.G. Electrochemically Enhanced Drug Delivery Using Polypyrrole Films. Materials 2018, 11, 1123.
15. Hepel, M.; Mahdavi, F. Application of the Electrochemical Quartz Crystal Microbalance for Electrochemically Controlled Binding and Release of Chlorpromazine from Conductive Polymer Matrix. Microchem. J. 1997, 56, 54–64.
16. Shamaeli, E.; Alizadeh, N. Kinetic studies of electrochemically controlled release of salicylate from nanostructure conducting molecularly imprinted polymer. Electrochim. Acta 2013, 114, 409–415.
17. Kontturi, K.; Pentti, P.; Sundholm, G. Polypyrrole as a model membrane for drug delivery. J. Electroanal. Chem. 1998, 453, 231–238.
18. Wu, Y.; Ruan, Q.; Huang, C.; Liao, Q.; Liu, L.; Liu, P.; Mo, S.; Wang, G.; Wang, H.; Chu, P.K. Balancing the biocompatibility and bacterial resistance of polypyrrole by optimized silver incorporation. Biomat. Adv. 2022, 134, 112701–112715.
19. Zeng, W.; Yu, M.; Chen, T.; Liu, Y.; Yi, Y.; Huang, C.; Tang, J.; Li, H.; Ou, M.; Wang, T.; et al. Polypyrrole Nanoenzymes as Tumor Microenvironment Modulators to Reprogram Macrophage and Potentiate Immunotherapy. Adv. Sci. 2022, 9, 2201703–2201720.
20. Wang, X.; Ma, Y.; Sheng, X.; Wang, Y.; Xu, H. Ultrathin Polypyrrole Nanosheets via Space-Confined Synthesis for Efficient Photothermal Therapy in the Second Near-Infrared Window. Nano Lett. 2018, 18, 2217–2225.
21. Sarkar, S.; Levi-Polyachenko, N. Conjugated polymer nano-systems for hyperthermia, imaging and drug delivery. Adv. Drug Deliv. Rev. 2020, 40, 163–164.

22. Yang, K.; Xu, H.; Cheng, L.; Sun, C.; Wang, J.; Liu, Z. In Vitro and In Vivo Near-Infrared Photothermal Therapy of Cancer Using Polypyrrole Organic Nanoparticles. Adv. Mater. 2012, 24, 5586–5592.
23. Bucharskaya, A.B.; Khlebtsov, N.G.; Khlebtsov, B.N.; Maslyakova, G.N.; Navolokin, N.A.; Genin, V.D.; Genina, E.A.; Tuchin, V.V. Photothermal and Photodynamic Therapy of Tumors with Plasmonic Nanoparticles: Challenges and Prospects. Materials 2022, 15, 1606.
24. Paúrova, M.; Taboubi, O.; Šeděnkova, I.; Hromădková, J.; Matouš, P.; Herynek, V.; Šefc, L.; Babič, M. Role of dextran in stabilization of polypyrrole nanoparticles for photoacoustic imaging. Eur. Polym. J. 2021, 157, 110634.
25. Liang, Y.; Mitriashkin, A.; Ting Lim, T.; Ting Lim, J. Conductive polypyrrole-encapsulated silk fibroin fibers for cardiac tissue engineering. J. Biomat. 2021, 276, 121008–121022.
26. Lee, R.-J.; Temmer, R.; Tamm, T.; Aabloo, A.; Kiefer, R. Renewable antioxidant properties of suspensible chitosan–polypyrrole composites. React. Funct. Polym. 2013, 73, 1072–1077.
27. Upadhyay, J.; Gogoi, B.; Kumar, A.; Buragohain, A.K. Diameter dependent antioxidant property of polypyrrole nanotubes for biomedical applications. Mat. Lett. 2013, 102–103, 33–35.
28. Varesano, A.; Vineis, C.; Aluigi, A.; Rombaldoni, F.; Tonetti, C.; Mazzuchetti, G. Antibacterial efficacy of polypyrrole in textile applications. Fib. Polym. 2013, 14, 36–42.
29. Upadhyay, J.; Kumar, A.; Gogoi, B.; Buragohain, A.K. Antibacterial and hemolysis activity of polypyrrole nanotubes decorated with silver nanoparticles by an in-situ reduction process. Mat. Sci. Eng. C 2015, 54, 8–13.
30. Soleimani, M.; Ghorbani, M.; Salahi, S. Antibacterial Activity of Polypyrrole-Chitosan Nanocomposite: Mechanism of Action. Int. J. Nanosci. Nanotechnol. 2016, 12, 191–197.
31. Nautiyal, A.; Qiao, M.; Edwin Cook, J.; Zhang, X.; Huang, T.-S. High performance polypyrrole coating for corrosion protection and biocidal applications. Appl. Surf. Sci. 2018, 427, 922–930.
32. Fan, S.; Wang, Z.; Liang, P.; Li, H.; Zhang, Y.; Fan, W.; Xu, G. Fabrication of polypyrrole coated superhydrophobic surfaces for effective oil/water separation. J. Mater. Res. Technol. 2022, 19, 4337–4349.
33. Menkuer, M.; Ozkazanc, H. Anticorrosive polypyrrole/zirconium-oxide composite film prepared in oxalic acid and dodecylbenzene sulfonic acid mix electrolyte. Progr. Org. Coat. 2020, 147, 105815–105825.
34. Morsi, S.M.M.; Abd El-Aziz, M.E.; Morsi, R.M.M.; Hussain, A.I. Polypyrrole-coated latex particles as core/shell composites for antistatic coatings and energy storage applications. J. Coat. Technol. Res. 2019, 16, 745–759.

35. Muro-Fraguas, I.; Sainz-García, A.; López, M.; Rojo-Bezares, B.; Múgica-Vidal, R.; Sainz-García, E.; Toledano, P.; Sáenz, Y.; González-Marcos, A.; Alba-Elías, F. Antibiofilm coatings through atmospheric pressure plasma for 3D printed surgical instruments. Surf. Coat. Technol. 2020, 399, 126163–126173.
36. Hathout, R.M.; Kader, A.; Metwally, A.; El-Ahmady, S.H.; Metwally, E.S.; Ghonim, N.A.; Bayoumy, S.A.; Erfan, T.; Ashraf, R.; Fadel, M.; et al. Dual stimuli-responsive polypyrrole nanoparticles for anticancer therapy. J. Drug Deliv. Sci. Technol. 2018, 47, 176–180.
37. Cheng, Y.; Tan, X.; Wang, J.; Wang, Y.; Song, Y.; You, Q.; Sun, Q.; Liu, L.; Wang, S.; Tan, F.; et al. Polymer-based gadolinium oxide nanocomposites for FL/MR/PA imaging guided and photothermal/photodynamic combined antitumor therapy. J. Control. Release 2018, 277, 77–88.
38. Michalik, A.; Rohwerder, M. Conducting polymers for corrosion protection: A critical view. J. Phys. Chem. 2005, 219, 1547–1559.
39. Paliwoda-Porebska, G.; Stratmann, M.; Rohwerder, M.; Potje-Kamloth, K.; Lu, Y.; Pich, A.Z.; Adler, H.-J. On the development of polypyrrole coatings with self-healing properties for iron corrosion protection. Corros. Sci. 2005, 47, 3216–3233.
40. Umoren, S.A.; Solomon, M.M. Protective polymeric films for industrial substrates: A critical review on past and recent applications with conducting polymers and polymer composites/nanocomposites. Prog. Mat. Sci. 2019, 104, 380–450.
41. Taheri, N.; Khoshsafar, H.; Ghanei, M.; Ghazvini, A.; Bagheri, H. Dual-template rectangular nanotube molecularly imprinted polypyrrole for label-free impedimetric sensing of AFP and CEA as lung cancer biomarkers. Talanta 2022, 239, 123146–123156.
42. Song, H.; Li, T.; Han, Y.; Wang, Y.; Zhan, C.; Wang, Q. Optimizing the polymerization conditions of conductive polypyrrole. J. Photopolym. Sci. Technol. 2016, 29, 803–806.
43. Rath, A.; Theato, P. Advanced AAO Templating of Nanostructured Stimuli-Responsive Polymers: Hype or Hope? Adv. Funct. Mater. 2020, 30, 1902959–1902975.
44. Cui, Z.; Coletta, C.; Dazzi, A.; Lefrançois, P.; Gervais, M.; Néron, S.; Remita, S. Radiolytic Method as a Novel Approach for the Synthesis of Nanostructured Conducting Polypyrrole. Langmuir 2014, 30, 14086–14094.
45. Taouil, A.E.; Mourad Mahmoud, M.; Lallemand, F.; Lallemand, S.; Gigandet, M.-P.; Hihn, J.-Y. Corrosion protection by sonoelectrodeposited organic films on zinc coated steel. Ultras Sonochem. 2012, 19, 1186–1195.
46. Apetrei, R.-M.; Carac, G.; Ramanaviciene, A.; Bahrim, G.; Tanase, C.; Ramanavicius, A. Cell-assisted synthesis of conducting polymer—Polypyrrole—For the improvement of electric charge transfer through fungal cell wall. Colloids Surf. B Biointerfaces 2019, 175, 671–679.

47. Yussuf, A.; Al-Saleh, M.; Al-Enezi, S.; Abraham, G. Synthesis and Characterization of Conductive Polypyrrole: The Influence of the Oxidants and Monomer on the Electrical, Thermal, and Morphological Properties. Int. J. Polym. Sci. 2018, 2018, 4191747.
48. Andriukonis, E.; Ramanaviciene, A.; Ramanavicius, A. Synthesis of Polypyrrole Induced by 3 and Redox Cycling of 4/3. Polymers 2018, 10, 749.
49. Leonavicius, K.; Ramanaviciene, A.; Ramanavicius, A. Polymerization Model for Hydrogen Peroxide Initiated Synthesis of Polypyrrole Nanoparticles. Langmuir 2011, 27, 10970–10976.
50. Grijalva-Bustamante, G.A.; Evans-Villegas, A.G.; del Castillo-Castro, T.; Castillo-Ortega, M.M.; Cruz-Silva, R.; Huerta, F.; Morallón, E. Enzyme mediated synthesis of polypyrrole in the presence of chondroitin sulfate and redox mediators of natural origin. Mater. Sci. Eng. C 2016, 63, 650–656.
51. Vernitskaya, T.V.; Efimov, O.N. Polypyrrole: A conducting polymer; its synthesis, properties and applications. Russ. Chem. Rev. 1997, 66, 443–457.
52. Fernandez, F.D.M.; Khadka, R.; Yim, J.-H. A comparative study between vapor phase polymerized PPy and PEDOT—Thermoplastic polyurethane composites for ammonia sensing. Polymer 2021, 217, 123463–123470.
53. Shafiqur Rahman, M.; Wasiu Adebayo, H.; Yahya, R.; Khairani Mohd Jamil, A.; Nabi Muhammad Ekramul Mahmud, H. One-step facile synthesis of poly(N-vinylcarbazole)-polypyrrole/graphene oxide nanocomposites: Enhanced solubility, thermal stability and good electrical conductivity. J. Macromol. Sci. Part. A 2019, 56, 384–391.
54. Kiefer, R.; Khadka, R.; Travas-Sejdic, J. Poly(ethylene oxide) in polypyrrole doped dodecylbenzenesulfonate: Characterisation and linear actuation. Int. J. Nanotechnol. 2018, 15, 689–694.
55. Brie, M.; Turcu, R.; Mihut, A. Stability study of conducting polypyrrole films and polyvinylchloride-polypyrrole composites doped with different counterions. Mater. Chem. Phys. 1997, 49, 174–178.
56. Kirsnytėa, M.; Jurkūnasa, M.; Kanclerisa, Ž.; Ragulisa, P.; Simniškisa, R.; Vareikisc, A.; Abraitienėa, A.; Požėlaa, K.; Whitesideb, B.; Tuinea-Bobeb, C.L.; et al. Investigation of in situ formed conductive polymer composite in adhesive matrix. Synt. Met. 2019, 258, 116181.
57. Khatoon, H.; Ahmad, S. A review on conducting polymer reinforced polyurethane composites. J. Ind. Eng. Chem. 2017, 53, 1–22.
58. Wampler, W.A.; Rajeshwara, K.; Pethe, R.G.; Hyer, R.C.; Sharma, S.C. Composites of polypyrrole and carbon black: Part III. Chemical synthesis and characterization. J. Mater. Res. 1995, 10, 1811–1822.
59. Hagler, J.R.; Peterson, B.N.; Murphy, A.R.; Leger, J.M. Performance of silk-polypyrrole bilayer actuators under biologically relevant conditions. J. Appl. Polym. Sci. 2019, 136, 46922–46932.

60. Otero, T.F. Biomimetic Conducting Polymers: Synthesis, Materials, Properties, Functions, and Devices. Polym. Rev. 2013, 53, 311–351.
61. Ansari, R. Polypyrrole Conducting Electroactive Polymers: Synthesis and Stability Studies. J. Chem. 2006, 3, 186–201.
62. Ansari Khalkhali, R. Electrochemical Synthesis and Characterization of Electroactive Conducting Polypyrrole Polymers. Russ. J. Electrochem. 2005, 41, 950–955.
63. Higgins, M.J.; McGovern, S.T.; Wallace, G.G. Visualizing Dynamic Actuation of Ultrathin Polypyrrole Films. Langmuir 2009, 25, 3627–3633.
64. Gribkovaa, O.L.; Kabanovaa, V.A.; Nekrasova, A.A. Electrochemical Polymerization of Pyrrole in the Presence of Sulfoacid Polyelectrolytes. Russ. J. Electrochem. 2019, 55, 1110–1117.
65. Tan, Y.; Ghandi, K. Kinetics and mechanism of pyrrole chemical polymerization. Synth. Met. 2013, 175, 183–191.
66. Krukiewicz, K.; Jarosz, T.; Zak, J.K.; Lapkowski, M.; Ruszkowski, P.; Bobkiewicz-Kozlowska, T.; Bednarczyk-Cwynar, B. Advancing the delivery of anticancer drugs: Conjugated polymer/triterpenoid composite. Acta Biomater. 2015, 19, 158–165.
67. Lo, M.; Diaw, A.K.D.; Gningue-Sall, D.; Aaron, J.-J.; Oturan, M.A.; Chehimi, M.M. Tracking metal ions with polypyrrole thin films adhesively bonded to diazonium-modified flexible ITO electrodes. Environ. Sci. Pollut. Res. 2018, 25, 20012–20022.
68. Gutiérrez-Pineda, E.; Alcaide, F.; José Rodríguez-Presa, M.; Bolzan, A.E.; Alfredo Gervasi, C. Electrochemical Preparation and Characterization of Polypyrrole/Stainless Steel Electrodes Decorated with Gold Nanoparticles. ACS Appl. Mater. Interfaces 2015, 7, 2677–2687.
69. Cysewska, K.; Karczewski, J.; Jasiński, P. The Influence of the Co-Dopant Dexamethasone Phosphate on the Electrodeposition Process and Drug-Release Properties of Polypyrrole-Salicylate on Iron. J. Electrochem. Soc. 2019, 166, G148.
70. Hua Lei, Y.; Seng, N.; Hyono, A.; Ueda, M.; Ohtsuka, T. Electrochemical synthesis of polypyrrole films on copper from phytic solution for corrosion protection. Corr. Sci. 2013, 76, 302–309.
71. Chebil, S.; Monod, M.O.; Fisicaro, P. Direct electrochemical synthesis and characterization of polypyrrole nano- and micro-snails. Electrochim. Acta 2014, 123, 527–534.
72. Borges, M.H.R.; Nagay, B.E.; Costa, R.C.; Sacramento, C.M.; Ruiz, K.G.; Landers, R.; van den Beucken, J.J.J.P.; Fortulan, C.A.; Rangel, E.C.; da Cruz, N.C.; et al. A tattoo-inspired electrosynthesized polypyrrole film: Crossing the line toward a highly adherent film for biomedical implant applications. Mater. Today Chem. 2022, 26, 101095–101099.
73. Saugo, M.; Flamini, D.O.; Brugnoni, L.I.; Saidman, S.B. Silver deposition on polypyrrole films electrosynthesised onto Nitinol alloy. Corrosion protection and antibacterial activity. Mat. Sci. Eng.

C 2015, 56, 95–103.

74. Wang, J.; Xu, Y.; Yan, F.; Zhu, J.; Wang, J. Template-free prepared micro/nanostructured polypyrrole with ultrafast charging/discharging rate and long cycle life. J. Power Sources 2011, 196, 2373–2379.
75. Chen, G.; Wang, Z.; Xia, D.; Zhang, L.; Hui, R.; Zhan, J. Whelk-like Helixes of Polypyrrole Synthesized by Electropolymerization. Adv. Funct. Mater. 2007, 17, 1844–1848.
76. Nezhadali, A.; Rouki, Z.; Nezhadali, M. Electrochemical preparation of a molecularly imprinted polypyrrole modified pencil graphite electrode for the determination of phenothiazine in model and real biological samples. Talanta 2015, 144, 456–465.
77. Huang, Z.; Li, X.; Pan, C.; Si, P.; Huang, P.; Zhou, J. Morphology-dependent electrochemical stability of electrodeposited polypyrrole/nano-ZnO composite coatings. Mater. Chem. Phys. 2022, 279, 125775–125787.
78. Bayat, M.; Izadan, H.; Molina, B.G.; Sánchez, M.; Santiago, S.; Semnani, D.; Dinari, M.; Guirado, G.; Estrany, F.; Alemán, C. Electrochromic Self-Electrostabilized Polypyrrole Films Doped with Surfactant and Azo Dye. Polymers 2019, 11, 1757.
79. Sui, J.; Travas-Sejdic, J.; Chu, S.Y.; Li, K.C.; Kilmartin, P.A. The actuation behavior and stability of p-toluene sulfonate doped polypyrrole films formed at different deposition current densities. J. Appl. Polym. Sci. 2009, 111, 876–882.
80. Syugaev, A.V.; Lyalina, N.V.; Maratkanova, A.N.; Smirnov, D.A. Molecular architecture of highly protective coatings of electrodeposited dodecyl sulfate-doped polypyrrole. Prog. Org. Coat. 2019, 131, 427–434.
81. Du, X.; Hao, X.; Wang, Z.; Ma, X.; Guan, G.; Abuliti, A.; Ma, G.; Liu, S. Highly stable polypyrrole film prepared by unipolar pulse electro-polymerization method as electrode for electrochemical supercapacitor. Synt. Met. 2013, 175, 138–145.
82. Joo, J.; Lee, J.K.; Lee, S.Y.; Jang, K.S.; Oh, E.J.; Epstein, A.J. Physical Characterization of Electrochemically and Chemically Synthesized Polypyrroles. Macromolecules 2000, 33, 5131–5136.
83. Zhang, W.; Pan, Z.; Yang, F.K.; Zhao, B. A Facile In Situ Approach to Polypyrrole Functionalization Through Bioinspired Catechols. Adv. Funct. Mater. 2015, 25, 1588–1597.
84. Sadat Eftekhari, B.; Eskandari, M.; Janmey, P.A.; Samadikuchaksaraei, A.; Gholipourmalekabadi, M. Surface Topography and Electrical Signaling: Single and Synergistic Effects on Neural Differentiation of Stem Cells. Adv. Funct. Mater. 2020, 30, 190792–190809.
85. Chandra Sekhar Rout, N.K. Conducting polymers: A comprehensive review on recent advances in synthesis, properties and applications. RSC Adv. 2021, 11, 5659–5698.

86. Kong, H.; Yang, M.; Miao, Y.; Zhao, X. Polypyrrole as a Novel Chloride-Storage Electrode for Seawater Desalination. Energy Technol. 2019, 7, 1900835–1900842.
87. Mettai, B.; Mekki, A.F.; Bekkar Djelloul Sayah, Z.; Moustefai Soumia, K.; Safiddine, Z.; Mahmoud, R.; Mehdi Chehimi, M. In situ chemical deposition of PPy/NDSA and PPy/DBSA layers on QCM electrodes: Synthesis, structural, morphological and ammonia sensing performances study. J. Polym. Res. 2018, 25, 95–107.
88. Yousef Elahi, M.; Bathaie, S.Z.; Kazemi, S.H.; Mousavi, M.F. DNA immobilization on a polypyrrole nanofiber modified electrode and its interaction with salicylic acid/aspirin. Anal. Biochem. 2011, 411, 176–184.
89. Flamini, D.O.; González, M.B.; Saidman, S.B. ; Saidman, S.B. sis and Characterization of Heparin-Doped Polypyrrole Coatings Using an Electrochemical Quartz Crystal Microbalance (EQCM). Port. Electrochim. Acta 2022, 40, 47–57.
90. Baek, S.; Green, R.A.; Poole-Warren, L.A. Effects of dopants on the biomechanical properties of conducting polymer films on platinum electrodes. J. Biomed. Mater. Res. Part. A 2014, 102A, 2743–2754.
91. Demoustier-Champagne, S.F.; Chrisitne, J.; Robert, J.; Roger, L. Electrochemically synthesized polypyrrole nanotubules: Effects of different experimental conditions, Electrochemically synthesized polypyrrole nanotubules: Effects of different experimental conditions. Eur. Polym. J. 1998, 34, 1767–1774.
92. Otero, T.F.; Sansiñena, J.M. Influence of synthesis conditions on polypyrrole-poly(styrenesulphonate) composite electroactivity. J. Electroanal. Chem. 1996, 412, 109–116.
93. Wang, P.-C.; Yu, J.-Y. Dopant-dependent variation in the distribution of polarons and bipolarons as charge-carriers in polypyrrole thin films synthesized by oxidative chemical polymerization. React. Funct. Polym. 2012, 72, 311–316.
94. Tabačiarová, J.; Mičušík, M.; Fedorko, P.; Omastová, M. Study of polypyrrole aging by XPS, FTIR and conductivity measurements. Polym. Degrad. Stab. 2015, 120, 392–401.
95. Holze, R. Overoxidation of Intrinsically Conducting Polymers. Polymers 2022, 14, 1584.
96. Debiemme-Chouvy, C.; Tuyet Mai Tran, T. An insight into the overoxidation of polypyrrole materials. Electrochem. Commun. 2008, 10, 947–950.
97. West, N.; Baker, P.G.L.; Arotiba, O.A.; Hendricks, N.R.; Baleg, A.A.; Waryo, T.T.; Ngece, R.F.; Iwuoha, E.I.; O’Sullivan, C. Overoxidized Polypyrrole Incorporated with Gold Nanoparticles as Platform for Impedimetric Anti-Transglutaminase Immunosensor. Anal. Lett. 2011, 44, 1956–1966.
98. Otero, T.F.; Padilla, J. Anodic shrinking and compaction of polypyrrole blend: Electrochemical reduction under conformational relaxation kinetic control. J. Electroanal. Chem. 2004, 561, 167–

171.

99. Otero, T.F.; Martinez, J.G. Activation energy for pol Activation energy for polypyrrole oxidation pyrrole oxidation: Film thickness influence. J. Solid. State Electrochem. 2011, 15, 1169–1178.
100. Ateh, D.D.; Navsaria, H.A.; Vadgama, P. Polypyrrole-based conducting polymers and interactions with biological tissues. J. R. Soc. Interface 2006, 3, 741–752.
101. Park, H.-W.; Kim, T.; Huh, J.; Kang, M.; Eun Lee, J.; Yoon, H. Anisotropic Growth Control of Polyaniline Nanostructures and Their Morphology-Dependent Electrochemical Characteristics. ACS Nano 2012, 6, 7624–7633.
102. Bocchetta, P.; Frattini, D.; Tagliente, M.; Selleri, F. Electrochemical Deposition of Polypyrrole Nanostructures for Energy Applications: A Review. Curr. Nanosci. 2020, 16, 462–477.
103. Zang, J.; Bao, S.-J.; Li, C.M.; Bian, H.; Cui, X.; Bao, Q.; Sun, C.Q.; Guo, J.; Lian, K. Well-Aligned Cone-Shaped Nanostructure of Polypyrrole/RuO2 and Its Electrochemical Supercapacitor. J. Phys. Chem. C 2008, 112, 14843–14847.
104. Mariano, A.; Lubrano, C.; Bruno, U.; Ausilio, C.; Bhupesh Dinger, N.; Santoro, F. Advances in Cell-Conductive Polymer Biointerfaces and Role of the Plasma Membrane. Chem. Rev. 2022, 122, 4–4552.
105. Schmidt, C.E.; Shastri, V.R.; Vacanti, J.P.; Langer, R. Stimulation of neurite outgrowth using an electrically conducting polymer. Proc. Natl. Acad. Sci. USA 1997, 94, 8948–8953.
106. Durgam, H.; Sapp, S.; Deister, C.; Khaing, Z.; Chang, E.; Luebben, S.; Schmidt, C.E. Novel degradable co-polymers of polypyrrole support cell proliferation and enhance neurite out-growth with electrical stimulation. J. Biomater. Sci. Polym. Ed. 2010, 21, 1265–1282.
107. del Pozo, J.L.; Rouse, M.S.; Patel, R. Bioelectric effect and bacterial biofilms. A systematic review. Int. J. Artif. Organs 2008, 31, 786–795.
108. Krukiewicz, K.; Janas, D.; Vallejo-Giraldo, C.; Biggs, M.J.P. Self-supporting carbon nanotube films as flexible neural interfaces. Electrochim. Acta 2019, 295, 253–261.
109. Liang, Y.; Cho-Hong Goh, J. Polypyrrole-Incorporated Conducting Constructs for Tissue Engineering Applications: A Review. Bioelctricity 2020, 2, 101–119.
110. Czerwinska-Główka, D.; Skonieczna, M.; Barylski, A.; Golba, S.; Przystaś, W.; Zabłocka-Godlewska, E.; Student, S.; Cwalina, B.; Krukiewicz, K. Bifunctional conducting polymer matrices with antibacterial and neuroprotective effect. Bioelectrochemistry 2022, 144, 10803–10817.
111. He, F.; Lycke, R.; Ganji, M.; Xie, C.; Luan, L. Ultraflexible Neural Electrodes for Long-Lasting Intracortical Recording. Science 2020, 23, 101387.

112. Khorrami, M.; Antensteiner, M.; Fallahianbijan, F.; Borhan, A.; Reza, M.; Annu, A. Conducting polymer microcontainers for biomedical applications. Int. Conf. IEEE Eng. Med. Biol. Soc. 2017, 23, 1869–1872.
113. Li, X.; Qiu, J.; Liu, X. Antibacterial Property and Biocompatibility of Polypyrrole Films Treated by Oxygen Plasma Immersion Ion Implantation. Adv. Mater. Interf. 2020, 7, 2000057.
114. Kumar, A.; Singh, R.K.; Agarwal, K.; Singh, H.K.; Srivastava, P.; Singh, R. Effect of p-toluenesulfonate on inhibition of overoxidation of polypyrrole. J. Appl. Polym. Sci. 2013, 130, 434–442.
115. Lunkes Ely, V.; Matiuzzi da Costa, M.; Pequeno de Oliveira, H.; Antonio Gomes da Silva Júnior, F.; Brayer Pereira, D.I.; Pereira Soares, M.; De Vargas, A.C.; Sangioni, L.A.; Cargnelutti, J.F.; Garcia Ribeiro, M.; et al. In Vitro algicidal effect of polypyrrole on Prototheca species isolates from bovine mastitis Algicidal activity of polypyrrole on Prototheca spp. Med. Mycol. 2020, 58, 1114–1119.
116. Děkanovský, L.; Elashnikov, R.; Kubiková, M.; Vokatá, B.; Švorčík, V.; Lyutakov, O. Dual-Action Flexible Antimicrobial Material: Switchable Self-Cleaning, Antifouling, and Smart Drug Release. Adv. Funct. Mater. 2019, 29, 1901880–1901890.
117. Forero López, A.D.; Loperena, A.P.; Lehr, I.L.; Brugnoni, L.I.; Saidman, S.B. Corrosion protection of AZ91D magnesium alloy by a duplex coating. J. Serb. Chem. Soc. 2020, 85, 1317–1328.
118. Forero López, A.D.; Lehr, I.L.; Brugnoni, L.I.; Saidman, S.B. Improvement in the corrosion protection and bactericidal properties of AZ91D magnesium alloy coated with a microstructured polypyrrole film. J. Magn. Alloys 2018, 6, 15–22.
119. Guo, Y.; Jia, S.; Qiao, L.; Su, Y.; Gu, R.; Li, G.; Lian, J. A multifunctional polypyrrole/zinc oxide composite coating on biodegradable magnesium alloys for orthopedic implants. Colloids Surf. B Biointerfaces 2020, 194, 111186.
120. Bhagya Mathi, D.; Gopi, D.; Kavith, L. Implication of lanthanum substituted hydroxyapatite/poly(n-methyl pyrrole) bilayer coating on titanium for orthopedic applications. Mater. Today Proc. 2020, 26, 3526–3530.
121. Zhou, W.; Lu, L.; Chen, D.; Wang, Z.; Zhai, J.; Wang, R.; Tan, G.; Mao, J.; Yu, P.; Ning, C. Construction of high surface potential polypyrrole nanorods with enhanced antibacterial properties. J. Mater. Chem. B 2018, 6, 3128–3135.
122. Martinez, A.L.; Brugnoni, L.I.; Flamini, D.O.; Saidman, S.B. Immobilization of Zn species in a polypyrrole matrix to prevent corrosion and microbial growth on Ti-6Al-4V alloy for biomedical applications. Prog. Org. Coat. 2020, 144, 105650–105660.
123. González, M.B.; Quinzani, O.V.; Vela, M.E.; Rubert, A.A.; Benítez, G.; Saidman, S.B. Study of the electrosynthesis of hollow rectangular microtubes of polypyrrole. Synt. Met. 2012, 162, 1133–

1139.

124. El Jaouhari, A.; El Asbahani, A.; Bouabdallaoui, M.; Aouzal, Z.; Filotás, D.; Bazzaoui, E.A.; Nagy, L.; Nagy, G.; Bazzaoui, M.; Albourine, A.; et al. Corrosion resistance and antibacterial activity of electrosynthesized polypyrrole. Synt. Met. 2017, 226, 15–24.
125. González, M.B.; Brugnoni, L.I.; Flamini, D.O.; Quinzani, L.M.; Saidman, S.B. Removal of Escherichia coli from well water using continuous laminar flow in a channel system containing PPy/Cu modified electrodes. J. Water Health 2018, 16, 921–929.
126. Puiggalí-Jou, A.; del Valle, L.J.; Alemá, C. Drug delivery systems based on intrinsically conducting polymers. J. Control. Release 2019, 309, 244–264.
127. Uppalapati, D.; Boyd, B.J.; Garg, S.; Travas-Sejdic, J.; Svirskis, D. Conducting polymers with defined micro- or nanostructures for drug delivery. Biomaterials 2016, 111, 149–162.
128. Michael Freedman, S.; Cui, X.T. Substrate Electrode Morphology Affects Electrically Controlled Drug Release from Electrodeposited Polypyrrole Films. Phys. Chem. Comm. 2014, 1, 15–25.
129. Wang, M.L.; Chamberlayne, C.F.; Xu, H.; Mofidfar, M.; Baltsavias, S.; Annes, J.P.; Zare, R.N.; Arbabian, A. On-demand electrochemically controlled compound release from an ultrasonically powered implant. RSC Adv. 2022, 12, 23337–23346.
130. Antensteiner, M.; Khorrami, M.; Fallahianbijan, F.; Borhan, A.; Reza Abidian, M. Conducting Polymer Microcups for Organic Bioelectronics and Drug Delivery Applications. Adv. Mater. 2017, 29, 1702576–1702587.
131. Glosz, K.; Stolarczyk, A.; Jarosz, T. Electropolymerised Polypyrroles as Active Layers for Molecularly Imprinted Sensors: Fabrication and Applications. Materials 2021, 14, 1369.
132. Czaja, T.; Wójcik, K.; Grzeszczuk, M.; Szostak, R. Polypyrrole–Methyl Orange Raman pH Sensor. Polymers 2019, 11, 715.
133. Boguzaite, R.; Ratautaite, V.; Mikoliunaite, L.; Pudzaitis, V.; Ramanaviciene, A.; Ramanavicius, A. Towards analytical application of electrochromic polypyrrole layers modified by phenothiazine derivatives. J. Electroanal. Chem. 2021, 886, 115132–115142.
134. Zhang, X.; Yang, W.; Zhang, H.; Xie, M.; Duan, X. PEDOT:PSS: From conductive polymers to sensors. Nanotechnol. Precis. Eng. 2021, 4, 045004–045024.
135. Sharma Pushpendra, K.; Sharma, P.K.; Gupta, G.; Singh, V.V.; Tripathi, B.K.; Pandey, P.; Boopathi, M.; Singh, B.; Vijayaraghavan, R. Synthesis and characterization of polypyrrole by cyclic voltammetry at different scan rate and its use in electrochemical reduction of the simulant of nerve agents. Synt. Met. 2010, 160, 2631–2637.
136. West, N.; Baker, P.; Waryo, T.; Ngece, F.R.; Iwuoha, E.I.; O’Sullivan, C.; Katakis, I. Highly sensitive gold-overoxidized polypyrrole nanocomposite immunosensor for antitransglutaminase

antibody. J. Bioact. Compat. Polym. 2013, 28, 167–177.

137. Landim, V.P.A.; Foguel, M.V.; Prado, C.M.; Sotomayor, M.P.T.; Vieira, I.C.; Silva, B.V.M.; Dutran, R.F. A Polypyrrole/Nanoclay Hybrid Film for Ultra-Sensitive Cardiac Troponin T Electrochemical Immunosensor. Biosensors 2022, 12, 545.
138. Zhang, X.; Tan, X.; Wang, P.; Qin, J. Application of Polypyrrole-Based Electrochemical Biosensor for the Early Diagnosis of Colorectal Cancer. Nanomaterials 2023, 13, 674.
139. Taheri, N.; Alizadeh, N. Vertically grown nanosheets conductive polypyrrole as a sorbent for nanomolar detection of salicylic acid. J. Pharm. Biomed. Anal. 2020, 188, 113365–113373.
140. Lo, M.; Ktari, N.; Gningue-Sall, D.; Madani, A.; Efremova Aaron, S.; Aaron, J.-J.; Mekhalif, Z.; Delhalle, J.; Chehimi, M.M. Polypyrrole: A reactive and functional conductive polymer for the selective electrochemical detection of heavy metals in water. Emergent Mater. 2020, 3, 815–839.
141. Senguttuvan, S.; Janaki, V.; Senthilkumar, P.; Kamala-Kannan, S. Polypyrrole/zeolite composite—A nanoadsorbent for reactive dyes removal from synthetic solution. Chemosphere 2022, 287, 132164–132172.
142. Biallozor, S.; Kupniewska, A. Conducting polymers electrodeposited on active metals. Synt. Met. 2005, 155, 443–449.
143. González, M.B.; Saidman, S.B. Electrodeposition of bilayered polypyrrole on 316 L stainless steel prevention. Prog. Org. Coat. 2015, 78, 21–27.
144. Zeybek, B.; Özçiçek Pekmez, N.; Kılıç, E. Electrochemical synthesis of bilayer coatings of poly(N-methylaniline) and polypyrrole on mild steel and their corrosion protection performances. Electrochim. Acta 2011, 56, 9277–9286.
145. Raman, S.; Ravi Sankar, A. Intrinsically conducting polymers in flexible and stretchable resistive strain sensors: A review. J. Mater. Sci. 2022, 57, 13152–13178.
146. Brito de Morais, V.; Crispilho Corrêa, C.; Martin Lanzoni, E.; Rodrigues Costa, C.A.; César Bof Bufon, C.; Santhiago, M. Wearable binary cooperative polypyrrole nanofilms for chemical mapping on skin. Mater. Chem. A 2019, 7, 5227–5234.
147. Liu, Y.-L.; Huang, W.-H. Stretchable Electrochemical Sensors for Cell and Tissue Detection. Angew. Chem. 2021, 60, 2757–2767.
148. Petty, A.J.; Keate, R.L.; Jiang, B.; Ameer, G.A.; Rivnay, J. Conducting Polymers for Tissue Regeneration in vivo. Chem. Mater. 2020, 32, 4095–4115.
149. Wang, C.; Xia, K.; Zhang, Y.; Kaplan, D.L. Silk-Based Advanced Materials for Soft Electronics. Acc. Chem. Res. 2019, 52, 2916–2927.

150. Chen, A.X.; Kleinschmidt, A.T.; Choudhary, K.; Lipomi, D.J. Beyond Stretchability: Strength, Toughness, and Elastic Range in Semiconducting Polymers. Chem. Mater. 2020, 32, 7582–7601.
151. Uzun, O.; Başman, N.; Alkan, C.; Kölemen, U.; Yılmaz, F. Investigation of mechanical and creep properties of polypyrrole by depth-sensing indentation. Polym. Bull. 2011, 66, 649–660.
152. Mazur, M. Preparation of three-dimensional polymeric structures using gas bubbles as templates. J. Phys. Chem. C 2008, 112, 13528–13534.
153. Qu, L.; Shi, G.; Chen, F.; Zhang, J. Electrochemical Growth of Polypyrrole Microcontainers. Macromolecules 2003, 36, 1063–1067.
154. Qu, L.; Shi, G. Hollow microstructures of polypyrrole doped by poly(styrene sulfonic acid). J. Polym. Sci. A Polym. Chem. 2004, 42, 3170–3177.
155. Turco, A.; Mazzotta, E.; Di Franco, C.; Santacroce, M.V.; Scamarcio, G.; Grazia Monteduro, A.; Primiceri, E.; Malitesta, C. Templateless synthesis of polypyrrole nanowires by non-static solution-surface electropolymerization. J. Solid. State Electrochem. 2016, 20, 2143–2151.
156. Chagas, G.R.; Darmanin, T.; Guittard, F. One-Step and Templateless Electropolymerization Process Using Thienothiophene Derivatives to Develop Arrays of Nanotubes and Tree-like Structures with High Water Adhesion. ACS Appl. Mater. Interfaces 2016, 8, 22732–22743.
157. McCarthy, C.P.; McGuinness, N.B.; Carolan, P.B.; Fox, C.M.; Alcock-Earley, B.E.; Breslin, C.B.; Rooney, A.D. Electrochemical Deposition of Hollow N-Substituted Polypyrrole Microtubes from an Acoustically Formed Emulsion. Macromolecules 2013, 46, 1008–1016.
158. Liu, D.; Uda, M.; Seike, M.; Fukui, S.; Hirai, T.; Nakamura, Y.; Fujii, S. Polypyrrole-coated Pickering-type droplet as light-responsive carrier of oily material. Colloids Polym. Sci. 2022, 300, 255–265.
159. Lee, J.I.; Hyo Cho, S.; Park, S.-M.; Kon Kim, J.; Kyeong Kim, J.; Woong Yu, J.; Kim, C.Y.; Russell, T.P. Highly Aligned Ultrahigh Density Arrays of Conducting Polymer Nanorods using Block Copolymer Templates. Nano Lett. 2008, 8, 2315–2320.
160. Li, X.; Malardier-Jugroot, C. Confinement Effect in the Synthesis of Polypyrrole within Polymeric Templates in Aqueous Environments. Macromolecules 2013, 46, 2258–2266.
161. Demoustier-Champagne, S.; Stavaux, P.-Y. Effect of Electrolyte Concentration and Nature on the Morphology and the Electrical Properties of Electropolymerized Polypyrrole Nanotubules. Chem. Mater. 1999, 11, 829–834.
162. Páramo-Garcia, U.; Avalos-Perez, A.; Guzman-Pantoja, J.; Díaz-Zavala, N.P.; Melo-Banda, J.A.; Gallardo-Rivas, N.V.; Reyes-Gómez, J.; Pozas-Zepeda, D.; Ibanez, J.G.; Batina, N. Polypyrrole microcontainer structures and doughnuts designed by electrochemical oxidation: An electrochemical and scanning electron microscopy study. e-Polymers 2014, 14, 75–84.

163. Mosch, H.L.K.S.; Akintola, O.; Plass, W.; Hoeppener, S.; Schubert, U.S.; Ignaszak, A. The specific surface versus electrochemically active area of the carbon/polypyrrole capacitor: The correlation of ion dynamics studied by an electrochemical quartz crystal microbalance with BET surface. Langmuir 2016, 32, 4440–4449.
164. Iordoc, M.; Bara, A.; Prioteasa, P.; Teisanu, A.; Marinescu, V. Electropolymerization of Conducting Polypyrrole on Carbon Nanotubes/Silicon Composite for Supercapacitor Applications. Rev. Chim. 2015, 66, 196–201.
165. Arjunan, T.V.; Senthil, T.S. Review: Dye sensitised solar cells. Mater. Technol. 2013, 28, 9–14.
166. Murad, A.R.; Iraqi, A.; Aziz, S.B.; Abdullah, S.N.; Brza, M.A. Conducting Polymers for Optoelectronic Devices and Organic Solar Cells: A Review. Polymers 2020, 12, 2627.
167. Sangiorgi, N.; Sangiorgi, A.; Tarterini, F.; Sanson, A. Molecularly imprinted polypyrrole counter electrode for gel-state dye sensitized solar cells. Electrochim. Acta 2019, 305, 322–328.
168. Saberi Motlagh, M.; Mottaghita, V.; Rismanchi, A.; Rafieepoor Chirani, M.; Hasanzadeh, M. Performance modelling of textile solar cell developed by carbon fabric/polypyrrole flexible counter electrode. Int. J. Sustain. Energy 2022, 41, 1106–1126.
169. Wu, J.; Wu, S.; Sun, W. Electropolymerization and application of polyoxometalate doped polypyrrole film electrodes in dye-sensitized solar cells. Electrochem. Comm. 2020, 122, 106879–106896.

Retrieved from https://encyclopedia.pub/entry/history/show/116988