

CONDUCTING POLYMERS-BASED ELECTROCHEMICAL PLATFORMS: FROM BIOSENSING TO ENERGY STORAGE

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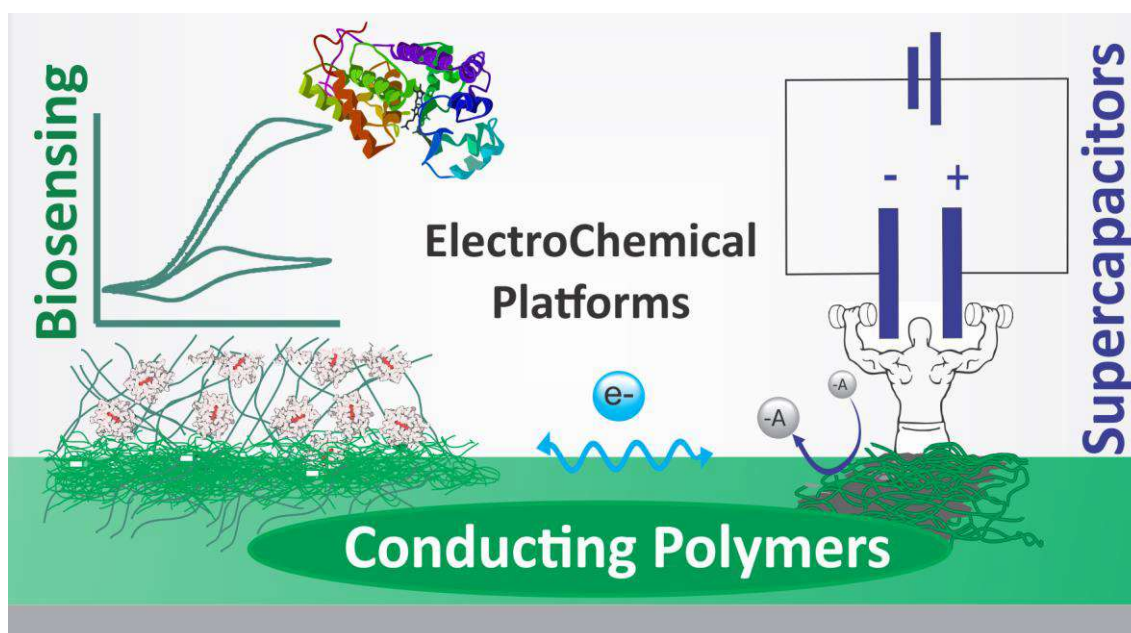
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Resumen Gráfico - Graphical abstract



Resumen

A partir su descubrimiento hacia los años 80, los polímeros conductores han sido ampliamente utilizados para la producción de materiales de electrodo en diferentes aplicaciones electroquímicas que van desde el sensado de especies en solución al almacenamiento de energía. La facilidad de síntesis, bajo costo y baja densidad son

algunas de las ventajas del empleo de estos materiales. En particular, su extensa aplicación en dispositivos de biosensado se basa en una serie de ventajas comparativas frente a otros materiales que incluyen la posibilidad de ofrecer entornos moleculares no desnaturizantes para las proteínas y otras biomoléculas y la capacidad de actuar como transductores fisicoquímicos de las señales químicas en respuestas eléctricas o simplemente mediar la transferencia electrónica entre biomoléculas redox y las plataformas de sensado. Por otro lado, la naturaleza polielectrolítica y la generación de cargas dependientes del potencial en estos materiales, producen enormes pseudocapacidades que los vuelven adecuados para su utilización en dispositivos de almacenamiento de carga tales como supercapacitores.

Abstract

Since its discovery in the 80's, Conducting Polymers have been extensively employed for the preparation of electrode materials in different applications from chemical and biochemical sensing to energy storage. Some of the comparative advantages of these materials are the facility of synthesis, low cost and low density.

Particularly, their wide-spread applications in biosensing devices are based on the possibility of providing non-denaturing environments for proteins and other biomolecules and the capacity of acting as physicochemical transducers of chemical signals into electrical out-puts or simply mediating the electron transfer between the biomolecules and the base electrode. On the other hand, the polyelectrolytic nature of conducting polymers and the origin of charges along the polymer chains depending on the applied potential render huge pseudocapacitances, making these materials adequate for the construction of energy storage devices, such as supercapacitors.

Palabras Clave: *Polímeros Conductores, Polianilina, Electroquímica, Sensado, Almacenamiento de Energía.*

Keywords: *Conducting Polymers, Polyaniline, Electrochemistry, Sensing, Energy Storage.*

1. Conducting Polymers

In 1977 Street and co-workers found that the electrical conductivity of films of polymeric sulfur nitride could be increased by bromine oxidation.¹ Some years later,

Heeger and MacDiarmid[†] applied the same procedure to polyacetylene films $(CH)_n$ yielding a 7 to 12-fold increment in the electrical conductivity.^{2,3} In analogy with the doping of semiconductors, this treatment with oxidizing agents was called p-doping (and n-doping for the chemical reduction). The same effect was observed in a series of organic polymers in the subsequent years. Furthermore, similar doping was achieved in the environment of an electrochemical cell, where the doping degree (oxidation degree) can be precisely controlled by electrochemical methods. On the other hand, at the early 80's, the electrochemical polymerization by oxidation of some aromatic monomers as aniline, thiophene and pyrrole was successfully developed, yielding polymer film-modified electrodes.

Nowadays, the polymers that can be reversible oxidized and reduced are referred to as *Electroactive Polymers*.⁴ These polymers are usually classified into *Conducting Polymers (CPs)* and *Redox Polymers* (**Figure 1**).⁵ Within the first class, they share a common characteristic: they present an extended double bond conjugation and, when they are in a partial oxidation (or reduction) state, they present metallic conductivity. Polyaniline (Pani), polypyrrole (PPy) and polythiophene (Pth) are famous examples of this kind of polymers. During the last 40 years, extensive families of polymers have been developed by employing derivatives of mentioned monomers, such as the case of the PEDOT, synthesized by oxidation of the 3,4-ethylenedioxythiophene.

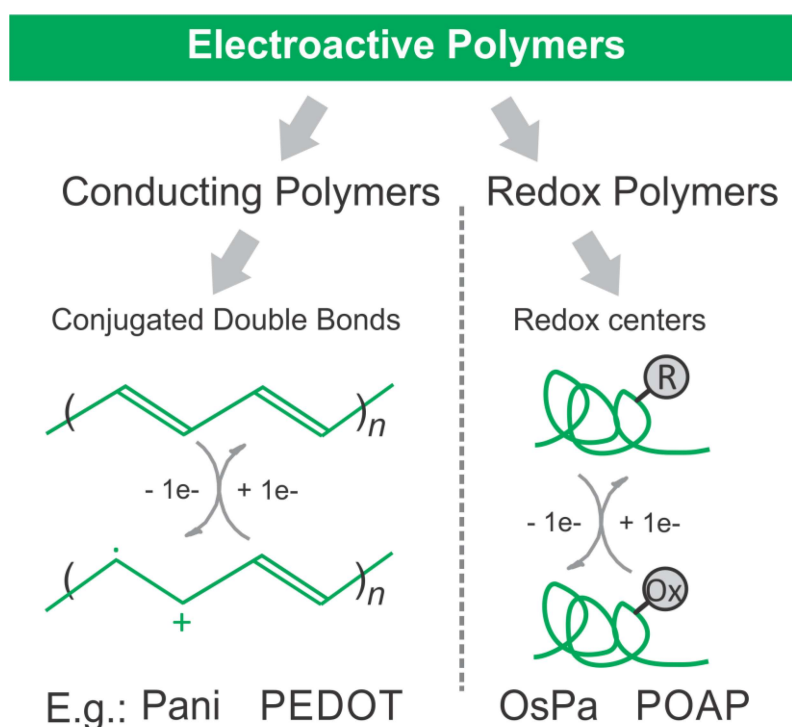


Figure 1. Classification and electrochemical reactions in Electroactive Polymers.

On the other hand, *Redox Polymers* are not conducting materials but they have redox centers in the polymer matrix. These centers can be part of the polymer structure, as in poly-o-aminophenol (POAP),⁶ or metallic complexes bound to the polymer chains, as in the case of the osmium complex-modified polyallylamine (OsPA).⁷

2.Pani for Energy Storage Applications

Owing to their excellent electronic and reversible electrochemical properties, CPs have been largely studied for decades.^{5,8} Pani has been one of the most investigated CPs as it presents high electronic conductivity, low-cost synthesis and good chemical stability.⁹⁻¹¹ Pani also presents other advantages such as the possibility of further chemical modifications¹² which have propelled its application in different areas.

Pani can be readily obtained by either chemical or electrochemical oxidation of aniline in acidic solutions.¹⁰ The product of the polymerization is an insoluble green solid with high electronic conductivity. This form is called *emeraldine* and it is an intermediate redox state. It can be reduced to *leucoemeraldine* and oxidized to *pernigraniline*.^{13,14} The basic structures of the different oxidation states were proposed by MacDiarmid and co-workers in the 80's.¹⁵ In the leucoemeraldine (L) state, the nitrogen atoms are secondary amines connecting benzenic rings. Leucoemeraldine is usually in its basic form, but at high acidic solutions it becomes protonated ($pK_a \approx 1$)¹⁶ and it is then referred as leucoemeraldine salt (LS). The oxidation of leucoemeraldine leads to the emeraldine form (E), where a quinone-imine structure is obtained by removing two electrons. Emeraldine can exist in its base form (EB) or protonated to the emeraldine salt (ES). Due to its particular chemical and electronic structure, the protonation equilibrium of the backbone nitrogen groups in the emeraldine form is difficult to describe. Moreover, this complex acid base behavior has been found to be dependent on the synthesis¹⁷ and experimental conditions.^{17,18} Consequently, a broad dispersion of pK_a values from 3 to 8 has been reported for the emeraldine form.^{16,18-20} The protonated emeraldine (emeraldine salt) corresponds to a dicationic structure (bipolaron), which can be internally transformed into a species with radical cations (polarons). In doped Pani, polarons are more stable than bipolarons and they are responsible for the high electronic conductivity.^{9,15,21}

Further oxidation of emeraldine yields the pernigraniline form (P), which is unstable in acidic solution.^{13,14,22,23} However, the redox transition between the L and E forms is highly reversible in acidic media (**Figure 2**).

The oxidation of leucoemeraldine to emeraldine promotes the generation of mobile charges and requires the ingress of a high proportion of anions in order to maintain the electroneutrality. In fact, the description of the redox response in Pani-like materials is complex as it strongly depends on the pH and the nature of the anions in solution.^{24–27} These characteristics have propelled the use of Pani in charge (and energy) storage applications, such as supercapacitors.

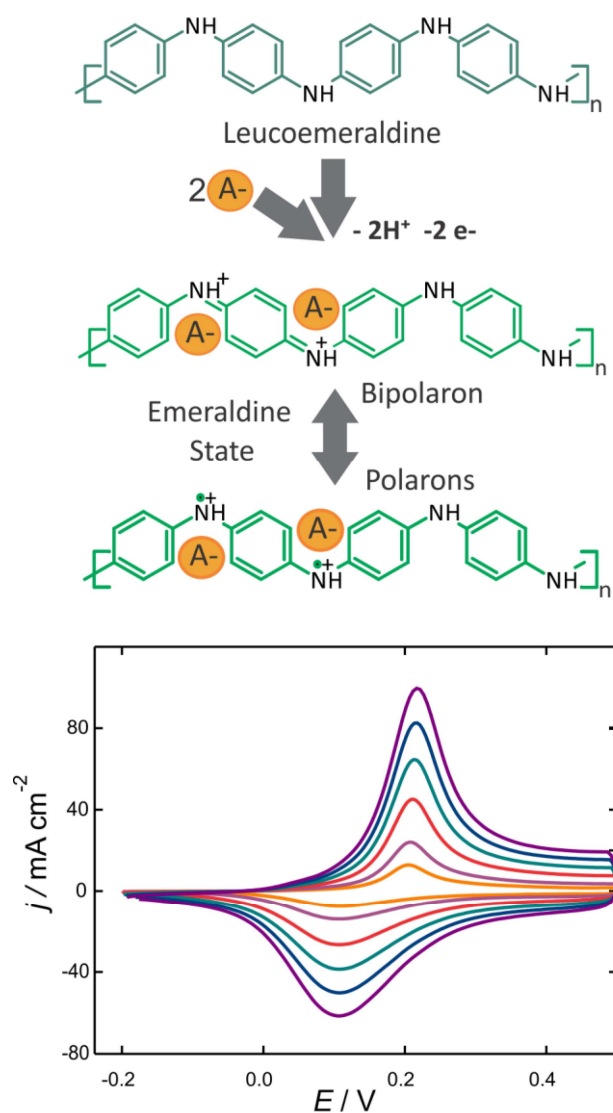


Figure 2. Chemical structures of the first redox transition of Pani. The oxidation implies the ingress of anions from the solution for charge compensation. The voltammetric response of a Pani-modified electrode (50 to 500 mVs⁻¹) in the potential range of this transition is presented at the bottom.

Supercapacitors (SCs) are electrochemical devices able to store charge by a nanometer-scale charge separation between the electrolyte and the electrode material.²⁸ Frequently, two main mechanisms of charge storage are recognized. In the double-layer mechanism (DL), the charge separation is performed within the so-called electrical double-layer established at the interface between the conducting phase and the electrolyte solution. On the other hand, the charge can be also stored by redox reactions, ion intercalation or ionic sorption promoted by polarization of the electrode. This mechanism involves a faradaic process, yielding the so-called pseudocapacitance, and typically happens in conducting polymers and metal oxides electrodes. Therefore, CPs can store charge not only by a DL mechanism but also by their rapid reversible electrochemical transformations (pseudocapacitance).²⁹

Particularly, Pani has become a promising material in energy storage applications as it has one of the highest theoretical specific pseudocapacitances (2000 F g^{-1}) caused by its fast and reversible redox transformations and high surface area.³⁰ Therefore, Pani has been extensively employed as material for SCs.^{31,32}

A serious problem in Pani-based SCs is the mechanical instability caused by the swelling and shrinkage during the doping/dedoping process, which can limit the storage performance and cyclability. This issue can be partially avoided by the incorporation of carbon nanomaterials to create hybrid nanocomposites with enhanced properties. A review on the layer-by-layer integration of Pani and carbon nanomaterials (carbon nanotubes and graphene oxide) for energy storage applications has been recently published.³³

3.PABA as a versatile building block

Although the electroactivity of Pani is excellent in acidic solution, it becomes poor at pH higher than 3, which represents a clear disadvantage for applications in neutral solutions, such as biosensing. Several strategies have been employed to improve the electroactivity in neutral media; e.g., the incorporation of metal nanoparticles,^{34,35} carbon nanomaterials^{36–38} or other complex anionic molecules capable of acting as dopants.^{39,40} Furthermore, the presence of amine groups in Pani were used in order to confer further chemical functionalization directed to cause an increase in the performance of Pani-containing biodevices. As an example, the formation of a phosphoramidate bond between terminal amino groups and phosphate groups of

artificial single-stranded DNA/RNA oligonucleotides (aptamers), has been employed in a variety of aptasensors.^{36,41} In the other approach, the desired functionality can be achieved by employing substituted anilines, whose additional chemical moieties act as self-dopants.⁴² An interesting example of substituted polyanilines is the polyaminobenzylamine (PABA), which bears additional pendant amine groups in the structure (**Figure 3**). The protonation of these groups confers additional charges to the polymer structure. Additionally, these pendant primary amines can be easily modified to introduce further chemical moieties or biorecognition elements in a higher extension than that reached in Pani.⁴³

Recently, the electrochemical copolymerization of aniline and 3-aminobenzylamine (ABA) has been reported to produce polymer films with higher electroactivity than Pani in neutral solutions.⁴⁴ Electrochemically stable films of variable thickness could be obtained by this method. The electroactivity in acid solution was higher for films with a high proportion of aniline, but films obtained from solutions with higher proportion of ABA presented better electrochemical response at neutral pH. The copolymer film-modified electrodes were used for successful mediation for the electro-oxidation of ascorbic acid at pH 7.

On the other hand, a method to obtain water dispersions of polyaminobenzylamine by chemical oxidation of ABA was also described.⁴⁵ This procedure does not involve laborious steps, yielding dispersions that remain stable in acidic solutions. The resulting polymer was characterized by diverse spectroscopic techniques and the dispersions were employed for the construction of layer-by-layer assemblies with polyanions. The LbL assemblies presented a linear dependence on the number of deposition cycles, whereas the spectroscopic measurements proved successful integration of the diverse counterparts within the films. These assemblies were found to be electroactive, both in acidic and neutral solutions, as a result of the combination of the doping effect by the polyanions, and the self-doping effect of the protonated amino groups in the PABA backbone. The PABA/polyanions LbL-modified electrodes also showed electrocatalysis of the ascorbic acid oxidation in neutral solutions.

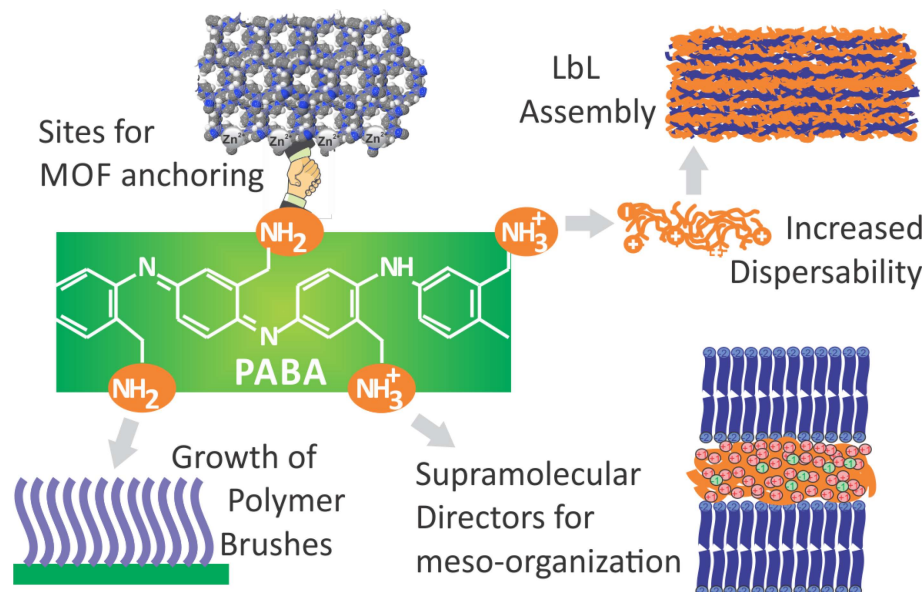


Figure 3. Chemical structure of PABA and schematic representation of the use of this building block in nanoarchitectonics.

This amino-appended polyaniline has resulted to be a versatile building block in electrochemical nanoarchitectonics as it could be satisfactorily integrated into different electroactive platforms (**Figure 3**).

The integration of PABA and a metal organic framework (MOF) for enhancing the oxygen reduction reaction (ORR) was recently demonstrated.⁴⁶ In that work, a ZIF-8 microporous film was grown over a PABA-modified electrode. The MOF layer acts as gas reservoir and, via a pre-concentration effect, causes the O₂ to be readily available for the electrochemical reaction of the CP film. The MOF layer was able to provide an efficient pathway for both oxygen diffusion (in the hydrophobic intragrain microporosity) and transport of counterions and solvent (in the intergrain mesoporosity). The extra amino groups in the CP backbone are presumably the responsible for the stable anchoring of the MOF layer via coordination with the zinc ions. The interplay between the electrocatalytic and anchoring properties of PABA and the oxygen storage capabilities of ZIF-8 yielded a new interfacial architecture exhibiting a more efficient response towards the ORR.

Other example of the use of PABA in the design of novel interfacial nanoarchitectures is the anchoring of a polymer brush by surface-initiated atom transfer radical polymerization (SI-ATRP),⁴⁷ using the extra amines of an electrochemically synthesized PABA film for the covalent crosslinking of an ATRP initiator. As PABA has extra pendant amino moieties, the grafting of the polyelectrolyte brush poly [2-

(methacryloyloxy)-ethyl-trimethylammonium chloride] (PMETAC) does not affect the backbone nitrogen atoms, which are implicated in the electronic properties. Moreover, as perchlorate anions interact very strongly with the quaternary ammonium pendant groups of PMETAC through ion pairing, the grafting adds the ion-actuation properties of the brush to the modified electrode, keeping the electroactivity. Thus, the conjugation of the electron transfer properties of the conducting polymer with the anion responsiveness of the integrated brush yielded perchlorate actuation of the electrochemical response (**Figure 4**).

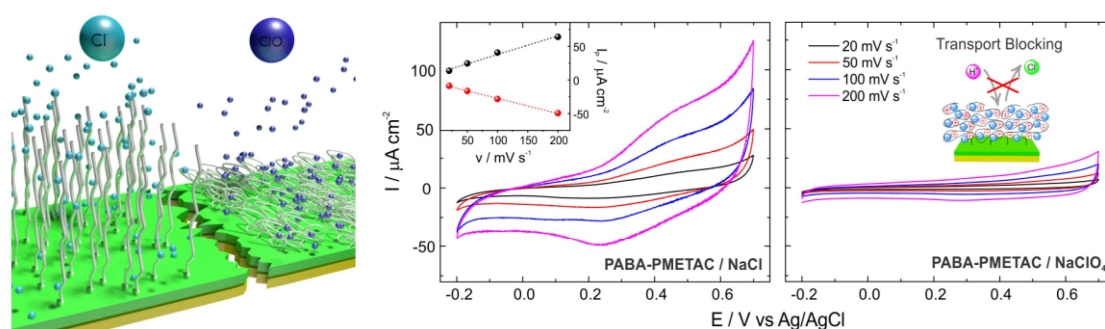


Figure 4. Schematic representation of the reversible conformational changes induced by perchlorate anions on the brush-modified PABA platforms (left) and voltammetric response in the presence and absence of these anions in solution (right).

In a completely different approach, the formation of electrostatic complexes between chemically synthesized PABA and an alkyl-phosphate was employed for the modification of electrodes with self-assembled electroactive polyelectrolyte-surfactant assemblies.⁴⁸ The complexes were deposited by spin-coating and the films were extensively characterized by X-ray-based techniques, showing a well-defined lamellar structure, directed by the strong interaction between the phosphate groups and the positive charged amine groups of PABA. These films also presented intrinsic electroactivity as proved by cyclic voltammetry, showing that PABA remains electroactive and ionic transport was still possible across the stratified hydrophobic coatings.

4. PEDOT platforms for biosensing

Conducting polymers-based platforms have been also extensively employed for the construction of biosensors²¹ and other biodevices⁴⁹ as they can provide an adequate

non-denaturing environment for the immobilization of enzymes and proteins and simultaneously they can act as physicochemical transducer of the chemical signals into a measurable electrical response, or simply mediate the electron transference to the electrode.^{21,50,51}

Pani, Ppy, Pth and their derivatives are the most representative polymers employed in the construction of bioelectrochemical devices due to their high electrical conductivity and excellent electrochemical activity, optical properties and chemical and thermal stability.⁵² One of the most promising polymers for bioelectronic application is a Pth derivative: poly(3,4-ethylenedioxythiophene) (PEDOT) (**Figure 5**). PEDOT was developed in 1988 at the Bayer AG research laboratories in Germany.⁵³ It shows high conductivity, good transparency and stability compared with PPy⁵⁴ and lower toxicity than Pani and Pth.⁵⁵ Moreover, unlike Pani that requires acid media to exhibit good electrochemical activity, PEDOT shows excellent conductivity and electroactivity in neutral solution. These properties combined with a good compatibility with biomolecules, such as enzymes, make PEDOT an appropriated polymer in the design of biosensing platforms. In addition, the remarkable conductivity of PEDOT allows the construction of bioelectrochemical devices without metallic substrates (all-plastic devices).^{56–58}

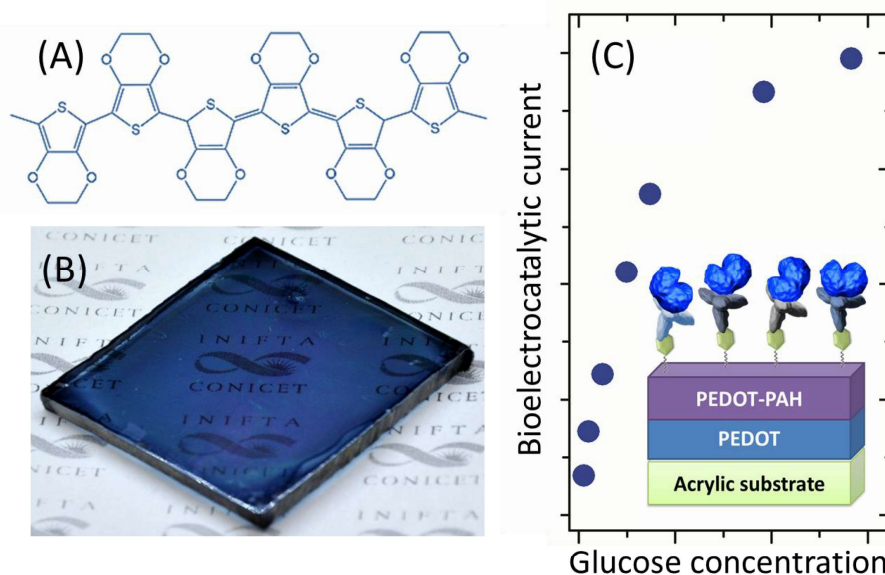


Figure 5. (A) Chemical structure of PEDOT. (B) Image of PEDOT/tosylate-modified plastic substrate. (C) Bioelectrocatalytic current for increasing glucose concentrations for a PEDOT–PAH composite all-plastic electrode modified with concanavalin A and glucose oxidase (scheme).

PEDOT is obtained by oxidative polymerization of 3,4-ethylenedioxythiophene (EDOT). There are different methods for the synthesis such as chemical polymerization,⁵⁹ electrochemical polymerization,⁶⁰ interfacial polymerization,⁶¹ vapor phase polymerization,⁶² being the first two the most widely employed. The electrical, mechanical and morphological properties of the resulting polymer depend on the synthesis procedures, reagents and solvents. In particular, the electrochemical deposition is a convenient way to obtain a polymeric-based material in a one-step procedure with superior electrochemical and mechanical properties and it also constitutes a simple method to control the thickness of the film. On the other hand, chemical polymerization is suitable for the large-scale production of materials with selected morphology.

In order to improve the stability and processability of the material, counter-anions are used to dope PEDOT, being the most common dopants polystyrene sulphonate (PSS) and iron/sodium tosylate salts. Commercially available water dispersible PEDOT: PSS was widely employed to fabricate PEDOT-based electrochemical biosensors using different methods to obtain the films such as dip-coating, spin-coating, drop-coating, inkjet-printing and screen-printing.⁶³ Furthermore, outstanding properties of PEDOT based materials are found when this polymer is combined with different components with synergistic effects. For instance, the incorporation of inorganic nanomaterials shows an improvement in the conductivity and mechanical stability of the films. Metal nanoparticles such as Ag, Au, and Pd have been deposited on the PEDOT surface to obtain platforms with large surface area and leading to an enhancement of the electrochemical response to molecular detection and the immobilization of enzymes in the polymer matrix. On the other hand, in the last years, carbon nanomaterials have received enormous attention because of their unique physicochemical properties. In particular, carbon nanotubes (CNTs), graphene (G), graphene oxide (GO) and reduced graphene oxide (rGO) have been exploited to improve the performance of biosensing platforms with potential applications in health-care sensors. As an example, amperometric enzymatic biosensors for glucose detection were extensively investigated.⁶⁴⁻⁶⁶ An electrode based on PEDOT nano-fibrous with electrodeposited palladium nanoparticles and immobilized glucose oxidase (GOx) was developed for glucose sensing in a wide linear concentration range.⁶⁶ A CNT/PEDOT electrode

incorporating (GOx) and alcohol dehydrogenase was obtained to determine glucose and ethanol concentrations with high sensitivity, showing that the combination of PEDOT and CNTs provides an optimized integration and synergic interaction of these materials.⁶⁴ Moreover, in order to obtain a simple and cost-effective biosensor for the determination of ascorbic acid, a one-step electrochemical process was developed for the construction of a PEDOT/G nanocomposite film with large surface area, high electrical conductivity and good biocompatibility. Non-enzymatic sensors were also developed, including Pd-decorated PEDOT nanospheres for H₂O₂ sensing⁶⁷ and a PEDOT/graphene oxide nanocomposite with copper nanoparticles, employed in glucose detection with negligible impact from dopamine, ascorbic acid, uric acid, sodium citrate and ethanol.⁶⁸

On the other hand, different redox mediators are usually employed to favor the electron transfer between the sensor active site and the electrode surface.^{69–71} Recently, an all-plastic biosensor based on PEDOT and a redox polymer was described.⁷² The synergistic combination of CPs and recognition-directed assembly to immobilize redox glycoenzymes was used for the construction of a large-area all-plastic biorecognizable electrode. To this end, PEDOT–poly(allylamine) (PEDOT–PAH) composites were prepared entrapping PAH in the polymer matrix. The PAH amine groups were modified using the divinylsulfone (DVS) cross-linker to anchor concanavalin A (Con A) and glucose oxidase to the composite surface with excellent results. The bioelectrocatalytic oxidation of glucose in the all-plastic platform was compared with the response obtained on a Con A-modified Au electrode with the same assembled, revealing an enhancement of the bioelectrocatalysis when GOx is assembled on the PEDOT–PAH composite (**Figure 5**).

5. Conclusions

Since their discovery, conducting polymers have excited and expanded the field of electrochemistry as they constitute non-expensive stable building blocks for the building up of a variety of electrochemically active components in numerous applications. Due to its particular electronic structure, they arise as light metal-free conducting materials able to be prepared by soft chemical methods, which made them immensely adequate for electrochemical nanoarchitectonics. Moreover, the reversible redox changes in these materials allow their application as active components of charge

storage devices or transducers of electrochemical signals in (bio)sensing platforms. Furthermore, they can be easily derivatized to produce tunable materials with enhanced properties and combined with organic/inorganic nanomaterials to generate more efficient electrode materials.

We have presented a series of examples of interesting electrochemical systems based on the integration of conducting polymers, some of them developed in our laboratory, to illustrate their potential. We hope this work encourages researchers to go deeper into the fascinating world of conducting polymers for electrochemical applications.

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