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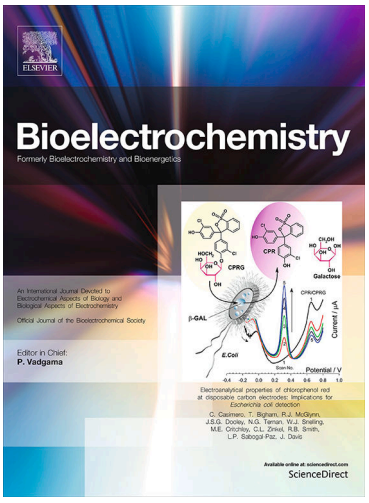

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FUNCTIONAL POLYMERS IN PHOTOELECTROCHEMICAL BIOSENSING

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Abstract

Photoelectrochemical (PEC) analysis is a detection technique that has gained a wide attention in sensing applications. PEC presents the advantages of high sensitivity, low background signal, simple equipment and easy miniaturization. In PEC detection, light is used as an excitation source while current or voltage is measured as the output detection signal. The ability to couple the PEC process with specific bioreceptors gives PEC biosensing a unique advantage of being both selective and sensitive. The growing interest in PEC bioanalysis has resulted in essential progress in its analytical performance and biodetection applications.

Functional polymers have different applications in the development of novel PEC biosensing platforms. Recently, the interest in polymer-based photoactive materials has emerged as they are efficient and less toxic alternatives to certain kinds of inorganic semiconductors and sensitizers. Moreover, molecularly imprinted polymers are a class of synthetic bioreceptors that are increasingly used in PEC bioanalytics.

In this review, we will provide an overview on functional polymer-based PEC biosensing approaches. Novel classes of polymers as photoactive materials are reviewed and selected applications are described. Furthermore, molecularly imprinted polymers in the development of smart and sensitive PEC bioanalytical strategies are discussed.

Keywords: photoelectrochemistry, polydopamine, phenothiazine, biosensor, bioanalysis, molecularly imprinted polymers.

1. Introduction: Principles, Materials and Examples of PEC biosensing

Photoelectrochemistry (PEC) is a vigorous and robust discipline focusing on the transformation of light energy into electrical and chemical energy. PEC is widely applied in the conversion of solar energy into electrical power as well as in environmental pollution remediation. The basic PEC process refers to photoelectrochemical reactions that happen when the incidence of photons on an electrode excites an electron within the electrode or excites a photoactive species in solution so that an electrochemical reaction occurs at the electrode. In both cases a current flows if the conditions are appropriate (Figure 1 A) [1].

In recent years, PEC biosensing approaches have been developed by combining a PEC platform with natural or synthetic bioreceptors, in which the light served as the excitation source and the current or voltage served as the signal readout [2–9]. The principle of PEC biosensing is based on monitoring the photocurrent/photovoltage changes resulting from the biological interactions between various recognition elements (enzymes, nucleic acids, antibodies, etc.) and their corresponding targets. Specifically, the biological recognition systems transfer the bioanalytical information (e.g., the concentration of the target analyte) into a variation in the photocurrent/photovoltage [5]. However, even if PEC devices based on the surface photovoltage readout, such as light addressable potentiometric sensors (LAPS), have been reported in literature, the main interest, nowadays, is on photocurrent-based PEC biosensing, as confirmed by the number of papers published on the subject (Figure 1B) over the past 10 years. The development of PEC enzyme biosensing platforms [10,11], nucleic acid PEC biosensing platforms [12–17] and PEC immunoassays [18] have been recently discussed in detail. Similarly, PEC aptasensors, which combine the sensitivity of the PEC detection mode with the high selectivity of aptamers [19], have been proposed for many applications [20,21]. Recently, molecularly imprinted polymers (MIPs) have emerged as an interesting class of biomimetic receptors in PEC biosensing. MIPs are prepared by polymerizing functional and cross-linking monomers around a target molecule. Because of their good stability, robustness, and easy preparation, MIPs have been used as recognition elements in manifold analytical areas including optical, electrochemical and PEC biosensing [22–28]. Conductive and non-conductive polymers have also been used for MIP fabrication.

The materials used as transducers in PEC biosensors can be grouped as follows: a) inorganic semiconductors, such as titanium dioxide (TiO_2), cadmium sulfide (CdS), zinc oxide (ZnO), cadmium telluride (CdTe), bismuth sulfide (Bi_2S_3); b) organic semiconductors, such as

phthalocyanine complexes, ruthenium complex, graphitic carbon nitride (g-C_3N_4), porphyrins and different kind of conducting polymers; c) hybrid semiconductors, i.e. those formed by the coupling of inorganic semiconductors with different band gaps, or organic and inorganic semiconductors, as well as the coupling of different metal or carbon nanomaterials with inorganic/organic semiconductors.

Conducting polymers are organic compounds that have both optical and electrical properties similar to those of inorganic semiconductors and metals [29–33], but which also exhibit the attractive properties associated with conventional polymers, such as ease of synthesis and flexibility in processing. Conducting polymers have been used as multifunctional materials in PEC biosensing. Polypyrrole, polytiophenes, polydopamine, polymer dots and others [34–38] have been used to design the photoactive sensing platform and the sensing strategy (i.e. photoactive labels of the biorecognition event). Conducting polymers have also been used to control and increase the immobilization efficiency of the bioreceptors onto the PEC transducers (acting as immobilization matrix).

The aim of this review is to summarize an updated survey on recent literature (2009-2019) on the role of organic polymer-based functional materials in PEC biosensing. The topic will be divided into two main different sections, taking into account different functions of polymers in PEC, i.e. the use of polymers in the design of the sensing platform and the use of polymers as receptors. However, as polymers are multifunctional materials, it was not always possible to make a clear separation of their functions. Selected classes of functional polymers for transducer and MIPs fabrication are described.

2. Functional polymers for the design of the biosensing platform

In the design of the PEC biosensing platform, polymers can play different roles. Functional polymers can be used as photoactive electrode materials, sensitizers as well as electron donors or electron acceptors. Furthermore, they can be used in labeling the biomolecular recognition event, modulating the photocurrent output at the transducer surface. Finally, due to the presence of functional groups, they can be used as immobilization matrix.

Many different types of conjugated polymers are of interest in the development of photoelectrochemical cells because of their semiconductive behavior and, as a result, of their photoactivity. Delocalization of the double bonds over the entire polymer molecule produces a valence and conduction band gap for most conducting polymers. Conductivity is related to

p-doping or n-doping of the conjugated backbone [32]. Polyanilines, polypyrrole, poly(phenylene-vinylenes), polythiophenes and their derivatives have been commonly used as photoactive materials and as photosensitizers and are still of great interest for developing novel electrochemical and PEC biosensing strategies [39–43]. Furthermore, two-dimensional carbon nitride (CN) has drawn increasing attention as a conjugated metal-free polymer [44], but many other novel polymeric molecules are continuously synthesized and investigated for PEC biosensing.

Indeed, conducting polymers are generally p-type photoactive materials [45]. Thus, when used to modify a conductive surface (i.e. an indium tin oxide (ITO), glassy carbon (GC) or gold (Au) electrode), the working principle of conjugated polymers-based PEC sensing is, basically, as follows [45]. Due to illumination, electrons are excited from the valence band to the conduction band of the polymer. The excited electrons are then transferred to a redox couple in solution. The hole left in the valence band is refilled from the conductive electrode by transfer of an electron from the electrode to the polymer.

Recently, a conjugated arylacetylene polymer [46] and a metal-organic polymer (phenylethnylcopper) [47] have been proposed as photocathodes in glucose sensing *via* glucose oxidase using dissolved oxygen as electron acceptor. In general, photocathodic bioanalysis is considered to be less sensitive to interference since the photocathodes are less prone to interacting with reductive substances (e.g., ascorbic acid) in the electrolyte medium.

Semiconducting polymer dots (Pdots) are proposed as functional photoactive materials [48] in PEC biosensing. Mainly, tetraphenylporphyrin (TPP)-doped conjugated polymer poly[(9,9-dioctyl-fluorenyl-2,7-diyl)-co-(1,4-benzo-{2,1',3}-thiadazole)] (PFBT) Pdots have been reported so far. TPP-doped PFBT Pdots have dimensions that can vary from few nanometers to tens of nanometers with different component ratios and sizes. It is reported that the surface properties of these Pdots are altered using selected components and surface functionalization is performed easily. TPP-doped PFBT Pdots have been immobilized on ITO electrode for the development of a photocathode acting as pH sensor, since, due to the presence of -COOH groups (protonated or deprotonated at different pH values), they are sensitive to pH variation [49]. At different pH values, conformational changes of Pdots occur that determine a variation in the diffusion of charges, with the cathodic photocurrent increasing with lowering the pH value. More recently, a signal-on and cathodic Pdots PEC biosensor toward telomerase (TE) activity in cell extracts has been reported [50]. Specifically, the sequential binding of a

capture DNA (cDNA), a telomerase-primer sequence (TS), and Au nanoparticles-labeled probe DNA (AuNPs-pDNA) on the electrode would place the AuNPs in proximity of the Pdots, leading to quenching of the cathodic photocurrent (Figure 2A). The subsequent extension of the TS by TE in the presence of deoxyribonucleoside triphosphates (dNTPs) would then release the AuNP-pDNA from the electrode, leading to the recovery of the photocurrent. Energy transfer between Pdots and AuNPs have also been applied for photocathodic monitoring of DNA hybridization [51]. Pdots modified surface can be modulated as function of the different electron donors/acceptors as well as by the coupling to inorganic semiconductors, especially quantum dots (i.e. CdTe QDs, CdS QDs) [52]. Interestingly, the direction and the amplitude of the resulting photocurrent (cathodic or anodic) are determined by the presence and the concentration of the electron acceptor and donor as well as by the bias potential applied to the electrode.

Conjugated polymers have also been used to design architecture of the PEC-bioassay, and both label free and label-based approaches have been reported (Figure 2 B-D). As an example, a perylene-based polymer was used to develop a red-light-driven DNA-based sensor for the monitoring of DNA methylation [53] due to its electrostatic intercalation efficiency in double-stranded DNA (Figure 2B). A cationic polyfluorene derivative (poly(9,9-bis(6'-(N,N,N,-trimethylammonium)hexyl)fluorene-co-alt-1,4-phenylene)bromide) (PFP) was used as label for human cell determination *via* the specific antibody-antigen interactions [54]. Upon adding cationic PFP, a favorable electrostatic interaction between cationic PFP and negatively charged cell membrane led to a turn-on detection signal for human cells. With a similar strategy, a cationic poly(phenylenevinylene) derivative was used to monitor microbial pathogens by binding the negatively charged membrane of pathogenic microorganisms [41]. Recently, PFP was used to monitor the activity of poly(ADP-ribose) polymerases (PARPs) [55] by using a dsDNA as capture probe immobilized on a ITO electrode. Poly(ADP-ribose) (PAR), a tumor marker molecule, consists of a large number of adenosine diphosphate (ADP) containing abundant phosphate groups which results much more negative charges than in dsDNA. Therefore, in the absence of PARP-1, the negatively charged active dsDNA combined only a little PFP, which resulted in weak photocurrent. By contrast, in the presence of PARP, hyper-branched PARs were generated under the activation of dsDNA by using NAD^+ as substrate, which subsequently combined much more PFP and led to a higher photocurrent.

Finally polymers can be used as sensitizers in PEC cell coupled to organic [56] or inorganic semiconductors [57,58]. Surface sensitization is the most common strategy to extend absorption of wide band-gap semiconductor into the visible light region. Sensitizers can be classified accordingly to the photoinjection process as Type I and Type II sensitizers [59]. In Type I photoinjection, electrons are transferred indirectly to the conduction band of a large band gap semiconductor after their excitation from the HOMO level to the LUMO level of the sensitizer. However, the excited state energy level of sensitizer should be higher than the semiconductor conduction band. Type II photoinjection involves a direct electron injection from the ground state of the sensitizer molecule to the conduction band of the semiconductor without any intermediation of excited sensitizer molecular states. In particular, catechol and its derivatives are known to be a Type II photoinjection sensitizers.

Some selected novel functional polymers proposed for the development of PEC biosensors are described in more details in the following paragraphs.

2.1 Polymer based on Phenothiazine

Phenothiazine (PTZ) is a hetero-tricyclic scaffold with the chemical formula $S(C_6H_4)_2NH$ discovered around two and half centuries ago. Since then this butterfly shaped molecule has drawn the attention of researchers from various disciplines, especially in medicine as it found to be useful as drugs for many different serious illness [60]. The photoluminescence, electroluminescence and electrochemical properties of this molecule can be significantly modified by derivatization of the PTZ moiety, so this electroactive molecule and its derivatives can provide a versatile platform for developing materials with wide range of functional applications [61,62]. The presence of electron-rich heteroatoms such as sulphur and nitrogen makes PTZ as efficient metal-free organic sensitizers used in PEC cells acting as a reducing and oxidizing agent [63,64]. PTZ-based polymer chemical synthesis is claimed to be more eco-friendly than that of other polymers [65] used in photoelectrochemical cell. Furthermore, the possibility of electropolymerization from an aqueous solution makes easier the development of the functional layer. For example, an electropolymerization strategy was introduced for preparation of phenothiazine polymeric film on ITO surface (PPT/ITO) [66] (Figure 2C). CdS QDs-functionalized PPT/ITO electrode (CdS/PPT/ITO) was proposed and applied for chlorpyrifos analysis, used as the model target organophosphorous pesticide. The phenothiazine polymeric film not only provided abundant positive groups to adsorb CdS QDs, but also worked as an effective charge acceptor and transporter to enhance the separation of

photo-generated charges, consequently improving the generation efficiency of PEC current. The thiocholine generated from acetylcholinesterase (AChE)-induced catalyzed hydrolysis of acetylthiocholine (ATCh) efficiently directed CdS QDs away from PPT/ITO *via* electrostatic repulsion, subsequently decreasing PEC current, whereas chlorpyrifos prohibited the generation of thiocholine through inhibiting AChE activity. As compared to the case where chlorpyrifos is absent, the enhanced PEC current is proportional to pesticide concentration [66]. Thus, this polymer can be used as sensitizers as well as to modify the surface of a conductive electrode, introducing specific charges or moieties in order to modify the electrode surface with proper functional molecules or nanomaterials. PTZ based photoactive layers have been also coupled to dihydronicotinamide adenine dinucleotide (NADH) determination and to dehydrogenase enzyme activity monitoring [67,68]. Many other PTZ dyes such as MB [69], Toluidine Blue O (TBO) [70], Nile Blue (NB) [71], Thionine [72,73], Azure A or Azure B [74] have been proposed for PEC analysis.

2.2 Polydopamine

In recent years, the number of studies concerning the functionalization of material surfaces *via* polydopamine (PDA) as bioinspired and biocompatible polymer coatings has dramatically increased [75–81].

Dopamine is a small-molecule compound acting as neurotransmitter in humans. The immediate precursor of dopamine, 3,4-dihydroxyphenylalanine (DOPA) is responsible for the excellent adhesive properties of *Mytilus edulis* foot proteins. PDA is a self-polymerization product of dopamine, which can be easily formed on any types of solid surfaces *via* spontaneous oxidative polymerization of dopamine in slightly alkaline aqueous solutions.

Although the clear structure of PDA has not yet been demonstrated, it has been widely used in various fields due to its unique physical and chemical properties. PDA structure incorporates many functional reactive groups such as indole, catechol, quinone [2–4]. Reactive groups at the surface of PDA film allow further derivatization with nitrogen and thiol residues through Schiff base formation or Michael-type addition and therefore can be used for immobilization of biologically active macromolecules, such as antibodies, enzymes, aptamers, DNA, etc. [82]. PDA also has a strong chelating ability with various metal ions such as Fe^{3+}, Ti^{4+}, Ca^{2+}, Mn^{3+}, Zn^{2+}, Cu^{2+}, etc. PDA has superior structural and thermal stability. It is not soluble in common solvents and only can be dissolved in strong basic aqueous solution. The absorption spectra of PDA covered the UV to visible area, and the absorbance decreased with the

increase of wavelength [83]. PDA has the remarkable redox characteristic of behaving as an oxidizing and reducing agent, having both, the oxidized o-quinone and the reduced o-hydro-quinone as subunits (as well as a semi-oxidized/semi-reduced form) [75]. The charge transfer and optical properties of PDA also enable its application in artificial photosynthesis and dye-sensitized solar cells [84]. In the development of PEC biosensors, PDA has been proposed as sensitizers of inorganic semiconductors, as electron donor/acceptors, as immobilization matrix and as biorecognition label.

When polymerized over a TiO_2 substrate, enediol ligands can bind to the under-coordinated surface of TiO_2 nanocrystalline, forming a dopamine-Ti charge transfer complex [80]. The surface modification of TiO_2 nanoparticles with these enediol ligands provides strong absorption bands in the visible region. PDA absorbs light and pumps its electron directly from the HOMO of the dye into the conduction band of TiO_2 (Type II sensitizer). The oxidized PDA (in the form of quinone or semiquinone species) is reduced and regenerated by a sacrificial reducer (electron donor) in solution. Without illumination, the current response of the semiconductor is low. Upon illumination, an apparently boosted photocurrent response appears, indicating the producing and transfer of photoelectron. The photocurrent obtained on PDA-coated photoelectrode is much higher, indicating efficient sensitization of the semiconductor by PDA film (Figure 3). Many examples of PDA-TiO_2 modified sensors and biosensors are reported in literature [85–89].

Besides being used as sensitizer, PDA is frequently used for the immobilization of the bioreceptors or other reagents over the PEC photoactive materials, including antibodies over ZnO [90], bismuth oxybromide (BiOBr) [91,92], ZnS-Ag_2S hetorojunctions, tungsten oxide (WO_3) [93], nile blue over hematite (α-Fe_2O_3) [94], enzymes over TiO_2 [95]. PEC sandwich immunosensor was designed for the detection of insulin based on WO_3/CdS/PDA co-sensitized and PDA@CNT conjugates for signal amplification. The CdS nanoparticles were first deposited on the WO_3 nanorods *via* sequential chemical bath deposition to form the WO_3/CdS structure to enhance photocurrent, and then modified with PDA to form the WO_3/CdS/PDA photosensitive structure. The PDA was used to immobilize insulin primary antibodies. The quinone functional groups of PDA are capable of covalent coupling to amine-terminated biomolecules (antibody) by Michael reactions. Meanwhile, insulin secondary antibodies were decorated by PDA@CNT conjugates for signal amplification [96]. Recently, AuNPs and PDA modified ITO electrode was used as biocathode substrate to immobilize the biomarker of prostate specific antigen antibody [97], (Figure 2D).

As already mentioned, behaving as an oxidizing and reducing agent, PDA was also used as electron donor as well as electron acceptor. As an example, PDA was proposed as electron donor for WS_2/black-TiO_2 photoactive material for histone acetyltransferase detection [98]. In another scheme PDA was proposed as electron donor in a sandwich assay for amino-terminal pro-B-type natriuretic peptides by using Bi_2WO_6/Ag_2S nanoparticles as photoactive material [40]. As already mentioned, CdS is a well-known narrow direct band gap (2.3 eV) semiconductor, and it has been widely studied as a photoanode in photoelectrochemical cells due to its excellent photoelectrochemical properties [99] and used for sensitizing TiO_2, ZnO or WO_3 [96,100]. It was found that benzoquinone could act as an electron acceptor of the photoexcited CdS, thus blocking the electron transfer of CdS to the conductive electrode, leading to decreased photocurrent. PDA has abundant benzoquinone groups, which acted as electron acceptors of the conduction band electrons of the photo-excited CdS, this strategy was proposed to detect dopamine [101].

3. Functional polymer as mimetic bioreceptors in PEC biosensing

Molecular imprinting technique (MIT) is a robust approach to improve the assay specificity, *via* the creation of tailor-made binding sites with memory of the shape, size and functional groups of the template molecules [102,103]. Molecularly imprinted polymers (MIPs), as alternative bioreceptors to build bioprobes and biosensors, have been widely proposed as an alternative to traditional approaches such as antigen-antibody binding. It is due to their high stability in different environmental conditions and capability of working in extreme environments (such as an organic solvent, acid or base, at high temperature and/or high pressure), low cost, ease of synthesis, and especially high selectivity. There are many methods of MIPs production and the reader is referred to Haupt [104], Kutner [31] and Piletsky [105] and other recent publications [106] for detailed explanations. Basically, in MIPs production, the target molecule acts as the template around which interacting and cross-linking monomers are arranged and co-polymerized. Initially, the monomers form a complex with the target molecule through non-covalent or covalent interactions. After polymerization, the template is removed. One of the frequently used methods for MIPs fabrication over an electrode is the electropolymerization of the polymer matrices dissolved in appropriate porogenic solvents. This bulk polymerization results in a porous polymer matrix with cavities (receptors) embedded in the polymer matrix. A subsequent removal of the template molecules leaves a cavity with complementary size, shape and chemical moieties to the template allowing the capture of analytes by the MIPs (~~Figure 4~~ Schematic 1) [107]. Other methods for preparing

MIP-modified PEC transducers is by drop-coating of a solution of a pre-prepared polymer, or by in situ thermal and UV polymerization [108,109] of a functional monomer and a template. Composite membranes containing a conducting material (e.g., carbon black), inside the MIP layer are also reported [110].

To prepare a MIP-based PEC biosensing platform, the choice of the photoactive material is crucial. For this reason, photoactive conjugated polymers such as polypyrrole, polythiophenes, polyanilines, poly(*p*-phenylenevinylene) have been used. However, approaches based on other kind of functional polymers have also been proposed.

In the following sections MIP-based PEC biosensor are revised considering the MIP preparation procedure (electroactive or non-electroactive monomer). Some selected applications of MIP-PEC sensors are summarized in Table 1.

3.1 Electropolymerization of functional polymers

Polypyrrole (PPy) is one of the most used conducting polymers for PEC biosensor development. The fabrication of MIP-PPy film on conductive substrate is performed by electrodeposition from a mixture of template molecule and pyrrole. In order to achieve the best sensitivity, it is necessary to regulate and to control the growth of PPy films. The thickness of the PPy film influences the property of the electrode by providing the amount of binding sites. The film thickness is governed by the amount of charge transferred during the electropolymerization. The overoxidation of the PPy layer can also influence the sensor performance.

PPy is a typically p-type semiconductor. Thus, when deposited on nanostructured n-type inorganic semiconductors (such as ZnO or TiO_2), the MIP-PPy layer may improve the sensitivity [39], allowing the formation of an hybrid semiconductor with p-n junction. Moreover, the π bond system of PPy can promote the separation of photogenerated electron-hole pair of the photoelectrode (when polymerized on TiO_2 [111], SnO_2 [112], ZnO [39,113]).

Furthermore, MIP-PPy modulate the photocurrent by interaction with the analyte [114]. Recently, selective Bisphenol S determination by using a PEC sensor consisting of a FTO electrode modified by ZnO nanorods (ZnO-NRs), functionalized by MIP-PPy electrodeposited on the surface (FTO/ZnO-NRs/MIP-PPy), was reported [39]. The current of the photoelectrode increased after incubation in Bisphenol S at “dark” conditions and it decreased under UV excitation. Thus, it was predicted that some photochemical processes

occurred between FTO/ZnO-NRs/MIP-PPy and Bisphenol S, when Bisphenol S was filling within PPy imprinted cavities. The MIP-PPy layer with special selectivity for 2,4-dichlorophenoxyacetic acid (2,4-D), a kind of carcinogen, was prepared on the Sn_3O_4 which was *in situ* decorated on a carbon fiber paper (Sn_3O_4@CFP) by electropolymerizing pyrrole in the presence of 2,4-D. The MIPPy/Sn_3O_4@CFP was further used for the detection of 2,4-D, where a photocurrent decrease was observed. This was attributed to the presence of 2,4-D which enhanced the steric hindrance of the electrode interface and blocked the electron transfer between the electrode and the solution [115], (Figure 54A). No electron or hole scavengers were need here, because the MIP sites created a microenvironment on the surface of Sn_3O_4 for the rebind and accumulate 2,4-D. Adsorption of 2,4-D based on shape selection and hydrogen bond recognition were occurred after incubating MIPPy/Sn_3O_4@CFP in the analyte solution. This paper demonstrated that the prepared PEC sensor can be used to detect 2,4-D directly in food samples.

Some electroactive functional monomers including p-aminothiophenol, *o*-phenylenediamine (*o*-PD) and others, electropolymerize forming non-conductive polymers [31,33] that can be still used for MIP-modified PEC platforms [116,117], (Figure 54B).

Recently, a MIP-PEC sensor based on bismuth sulfide (Bi_2S_3) was described for the determination of the plasticizer dioctyl phthalate. Bi_2S_3 was prepared on the surface of an ITO electrode. MIP films, containing *o*-PD as the functional monomer and dioctyl phthalate as the template molecule, were electropolymerized onto the surface of Bi_2S_3/ITO *via* cyclic voltammetry. The photocurrent decreased after adsorption of dioctyl phthalate, thereby indicating that the dioctyl phthalate blocked the imprinted cavities on the MIP, and at the same time the MIP film can rebind the molecules of analyte [118].

By using propoxur as a template molecule and *o*-PD as a functional monomer, a MIP film was formed by electropolymerization on $AgBiS_2$/Bi_2S_3 composite-modified Ti electrode. The template molecules of propoxur in the polymer combine with functional monomers of *o*-PD by hydrogen bonds. The specific binding of propoxur with the imprinted cavity hindered the electron donor from passing through the cavity to the surface of the MIP/$AgBiS_2$/Bi_2S_3/Ti, resulting in a decrease in photocurrent [119].

A microfluidic paper-based analytical device (μPAD) was presented with ZnO nanoflowers (ZnO NFs) constructed on conductive rGO substrates and *o*-PD electropolymerized at AuNPs/μPAD as two functional parts on the cellulosic matrix. Ferrocenemethanol can be

directly oxidized by photogenerated holes from the ZnO NFs under UV. The photooxidation products flowed to MIP membranes along the hydrophilic channel *via* capillary action. When analytes (L-glutamic acid or L-cysteine) were rebound to the recognition sites of MIP membranes due to the specific spatial effect, the target molecules inhibited the reduction reaction between electrons and photo-oxidation products, resulting in the enhancement of PEC signal [120]. The porosity of MIP/AuNPs/μPAD decreased rapidly (compared prior MIP modification), which could provide the important basis for signal amplification because the solution containing photo-oxidation products was inhibited to react with electrons from rGO electrode after target molecules were added to detection zone.

3.2 Polymerization of non-electroactive functional monomer

Although electropolymerization is one of the most common methods to prepare MIPs for PEC biosensing, there are other variations that involve thin film on the surface of a nano-support, usually with a chemically or physically adsorbed initiator, an approach that affords analyte access to the trapping cavities. The molecular imprinting process typically involves the copolymerization of a functional monomer (or a series of functional monomers), a cross-linker and an initiator in the presence of template molecules. For example, 2,2-azobisisobutyronitrile (AIBN) as the initiator together with ethylene glycol dimethacrylate (EGDMA) as a crosslinker, are often used for a free radical polymerization initiated by UV irradiation. In other cases, MIPs are pre-prepared in solution and then casted onto the electrode surface. The monomer possesses special functional groups to bind with the template molecules.

Different functional monomer have been proposed for PEC biosensor development such as acrylamide for the PEC determination of perfluorooctane sulfonate [121] and perfluorooctanoic acid [122] (Figure ~~5~~4C), as reported in Table 1, or 4-vinylpyridine for the determination of Bisphenol A [123,124]. Recently, methacrylic acid as a functional monomer, EGDMA and AIBN were mixed with template molecules of fumonisin B_1 [125] (Figure ~~5~~4D) or α-Solanine [126] and dropped on photoelectrodes for the preparation by UV polymerization of MIP/GO/CdS/CS/ITO and MIP/CdS/Pdots/CS/ITO, respectively. In both cases, ascorbic acid was used as a sacrificial electron donor. When the MIP-PEC sensors were eluted, their photocurrent response was significantly promoted, which was based on the fact that template molecule was washed away from MIP, and electron donors entered the caves and accelerated the electron transfer. The electron donor in the solution could provide

electrons to the valence band of the photoelectrode to trap holes through the cavities of the MIP membrane, thus forming a loop for photocurrent generation. The photocurrent response of MIP-PEC sensors was further decreased, because the electron-holes were blocked after incubating in the template molecules solution. The use of methacrylic acid was reported to result in a polymer with high surface area and high adsorption capacity towards adsorption of template molecules attributed to carboxyl groups of methacrylic acid. It was assumed that the template molecule could interact with monomer residues of methacrylic acid by means of hydrogen bonding. The combination with acetonitril may result in higher interaction with template molecule, thus creating more selective binding sites during polymer synthesis [127].

In combination to MIP, other advanced functional materials such as CNTs, graphene, QDs, could be integrated as functional modifiers for improving analyte detection depending on the transduction method.

A paper-based MIP-PEC sensor was developed for the detection of S-fenvalerate. The MIP-PEC strategy was based on CdTe QDs MIP (CdTe QDs@MIP). S-fenvalerate was dissolved in toluene and acrylamide as functional monomer together with AIBN as initiator were added under continuous stirring, followed by the addition of EGDMA as crosslinker. Then CdTe QDs cultivation with EDC-NHs was added and stirred. The paper-based PEC sensor was fabricated by immobilizing CdTe QDs@MIP on paper-based screen-printed working electrodes *via* AuNPs (CdTe QDs@MIPs/Au-WE), which were electrodeposited on the surface of working electrode to improve the electron transfer efficiency for high sensitivity. The photocurrent of the CdTe QDs@MIPs/Au-WE in the presence of S-fenvalerate decreased evidently compared to that of the CdTe QDs/Au-WE. This may result from the conjugation of MIPs and S-fenvalerate, which could effectively prevent the modified electrode from photochemical etching~~, and made the PEC sensor more stable~~ [128].

Carbon aerogel (CA) was prepared by sol-gel process at ambient pressure drying. The CA is an interconnected 3D network structure and possesses a high specific surface area, a suitable pore size distribution and distinguished electrical conductivity, which may facilitate the separation of photo-generated electron-hole pairs and promote the charge transfer in the photoelectric oxidation reaction. A novel PEC sensing platform with excellent photochemical catalysis and molecular recognition capabilities was fabricated on the CA with a convenient surface modification of molecularly imprinted TiO_2 (denoted as MIT/CA) for the atrazine monitoring. Ti and atrazine were dissolved in toluene-ethanol mixture, and then vigorously

stirred. After that, the solution was diluted with water-saturated toluene and continuously stirred to get a sol-gel solution. The CA was immersed into the above-mentioned sol-gel for 15 min, rinsed with toluene, hydrolyzed in water and dried in nitrogen atmosphere, producing a modified CA whose surface was covered with a TiO_2 layer containing the template molecule of atrazine. The relatively strong photocurrent response of the MIT/CA electrode indicated a better conductivity, accelerated electron transfer, lowered recombination of photogenerated electrons-holes and enhanced photoelectric conversion efficiency of electrode compared to TiO_2/CA electrode. The photocurrent response of the MIT/CA was obviously enhanced in the presence of atrazine [110].

4. Conclusions

In this Review, we have discussed the current developments in PEC biosensing technology, using different functional polymers. Both conducting and non-conducting polymers have been proposed as functional polymers in the development of PEC biosensors. This is due to the different roles that polymers can play in the assembly of a PEC biosensor, from photoactive materials and photosensitizers to bioreceptors. Conducting polymers such as PPy have been used as organic semiconductors for the development of photoelectrode. Conducting polymers, such as PDA, have been proposed as photosensitizer of inorganic semiconductor in many PEC biosensing approaches. However, both conductive and non-conductive monomers have been investigated for obtaining imprinted polymers obtaining interesting performance for different analytical applications. The development and application of novel photoelectric active materials, in which more stable detection signal can be obtained by choosing environmentally friendly non-toxic photoactive materials is of a great interest. The way in which the recognition event is integrated into the PEC system is critical for the establishment of a successful bioanalysis. The existence of nonspecific adsorption and oxidation/reduction of interferents resulting in low reproducibility and selectivity can be a major problem. An important progress in the synthesis and application of highly selective MIP-based biosensors has been reported consistently in the literature within recent years. The construction of MIP-modified μPAD opens the rich possibility for designing more efficient PEC analytical strategy with advantages of high reproducibility, unique stability, high selectivity and promising application potential as a portable and smart device. Nevertheless, the analysis of real samples and the validation of the obtained results with standard analytical techniques should be always accomplished. Furthermore, a detailed understanding of the theoretical basis of the observed phenomena in the PEC assay should be always described. These steps should help to identify

a more rigorous and reliable PEC-based test exploiting different innovative materials and assay formats.

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Figure Captions

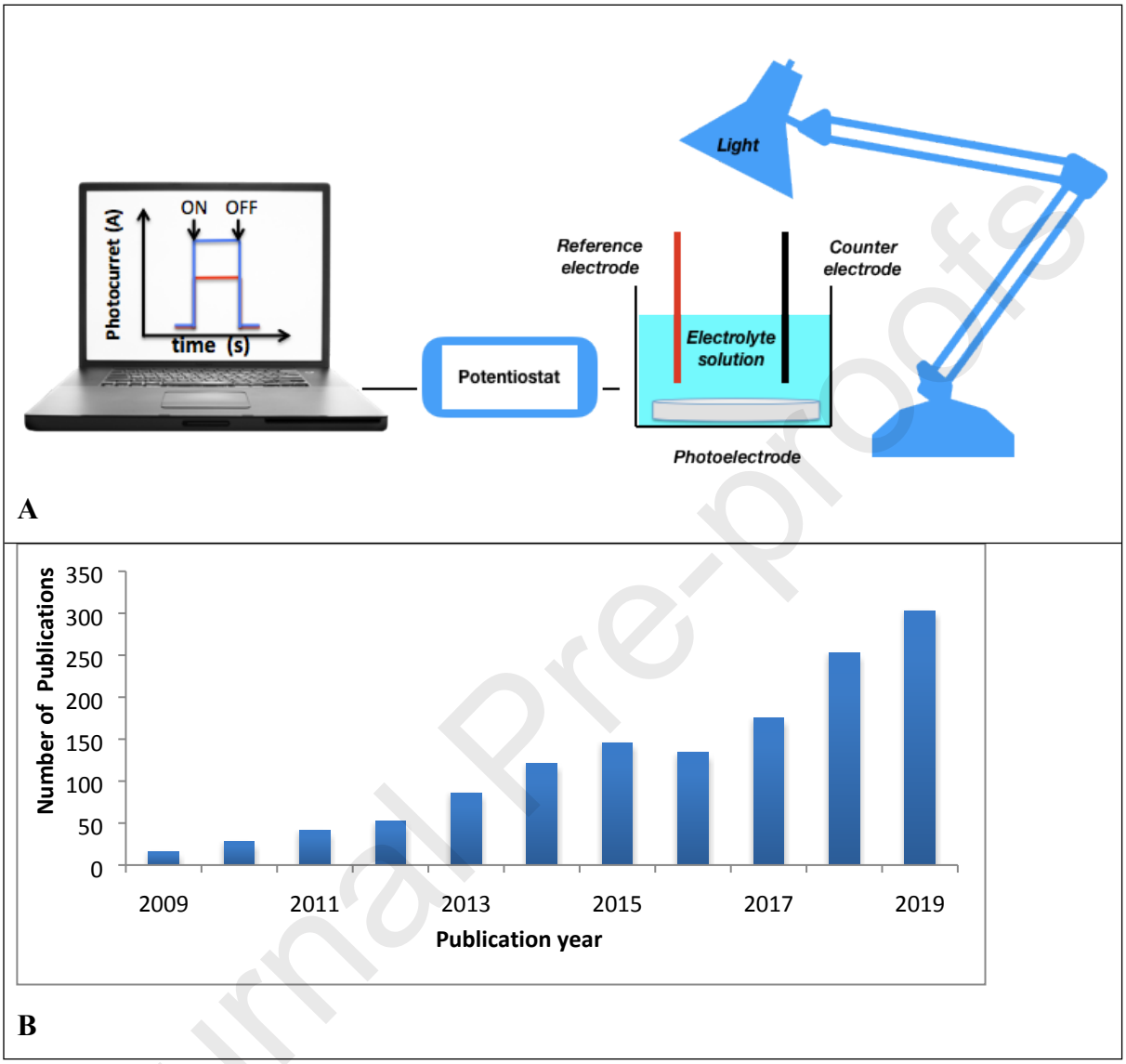
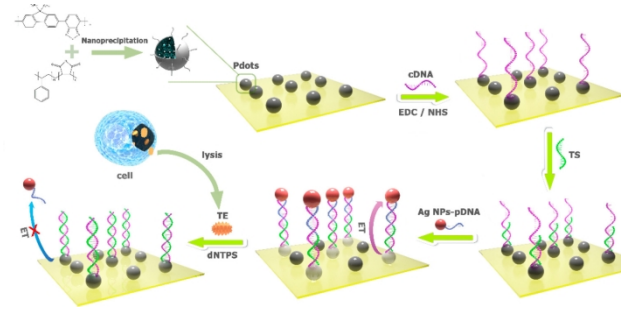


Figure 1: A) Scheme of a classical PEC experimental setup; B) Graph of a search on the term ‘‘PEC biosensor’’ during the period 2009 to 2019, using the SciFinder® system



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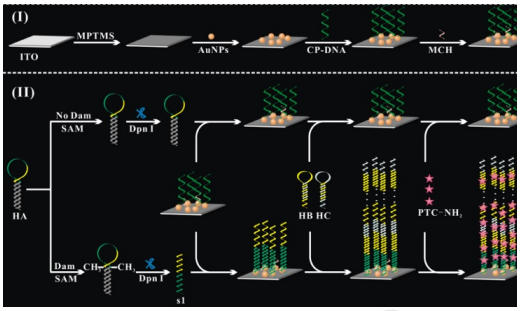

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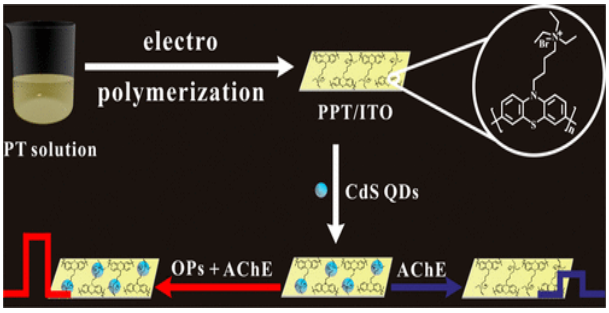

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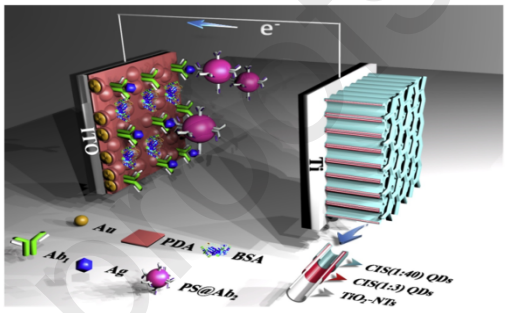


D

Figure 2: Examples on the use of polymers for the design of the PEC platform. **A)** Signal-On ET-Based Photocathodic Bioanalysis of TE Activity in Cell Extracts. Reprinted with permission from ref. [129]; **B)** Illustration of the Perylene-Based PEC Sensor for Dam MTase Sensitive Detection Based on Target-Triggered Hybridization Chain Reaction: the perylene based polymer (PTC-NH_2) could specifically/efficiently intercalate into the dsDNA grooves. Reprinted with permission from ref. [53]; **C)** The phenothiazine (PPT) polymeric provided abundant positive groups to adsorb CdS QDs; the thiocholine generated from acetylcholinesterase (AChE)-induced catalyzed hydrolysis of acetylthiocholine (ATCh) efficiently directed CdS QDs away from PPT/ITO, whereas chlorpyrifos prohibited the generation of thiocholine through inhibiting AChE activity. Reprinted with permission from ref. [66]; **D)** PDA acting as immobilization layer in a PEC immunosensor coupling photoanode with biocathode. Reprinted with permission from ref. [97].

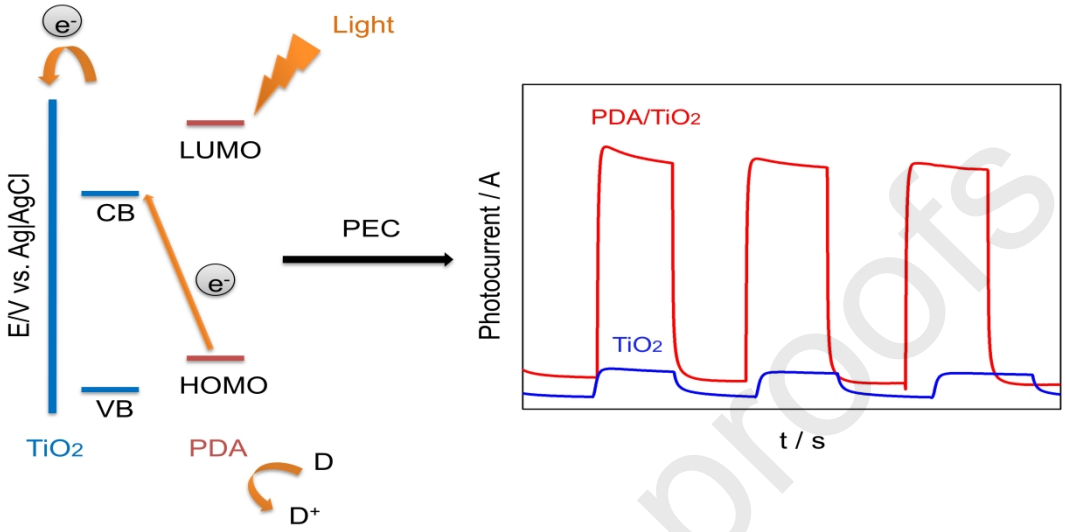
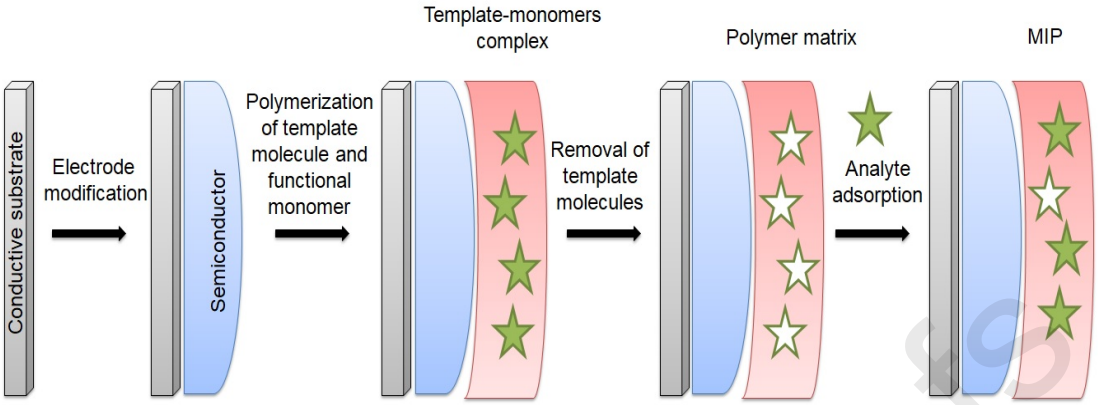


Figure 3: Schematic illustration of PEC response after modification of the TiO_2 with a PDA layer. CB – conduction band, VB – valence band, D – electron donor.



~~Figure 4~~ Schematic 1: ~~Schematic~~ Illustration of fabrication of MIP ~~PEC~~ sensor.

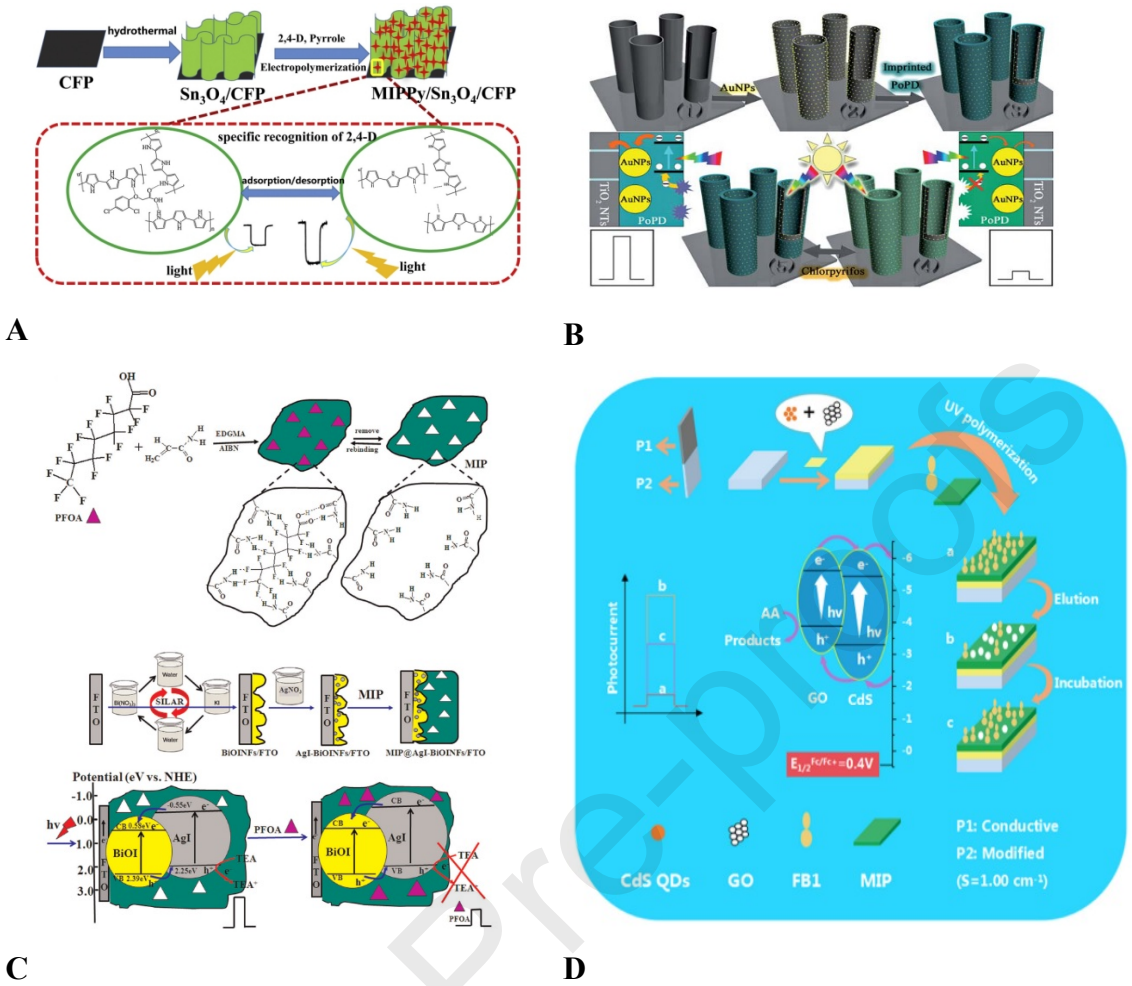
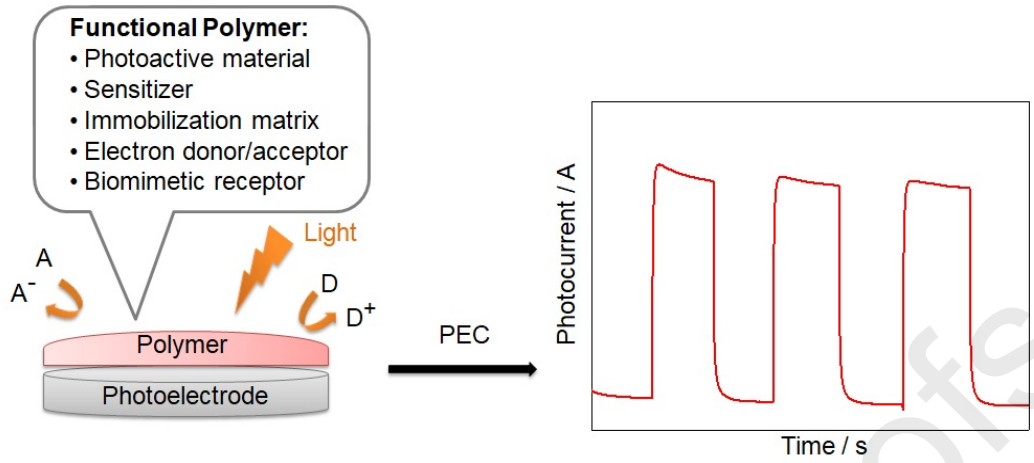


Figure 54: Examples on the use of MIPs for the design of the PEC platform. **A)** Illustration of the electropolymerization of pyrrole and MIPPy/Sn_3O_4@CFP creation for 2,4-D detection. Reprinted with the permission from ref. [115]; **B)** Illustration for fabrication of the MIP–AuNPs/TiO_2 NTs PEC sensor for chlorpyrifos detection, using electrochemical polymerization of *o*-PD. Reprinted with the permission from ref. [116]; **C)** Iillustration of the formation process of the MIPs using acrylamide AIBN and EGDMA, and the principle of PEC determination of PFOA using MIP@AgI–BiOINFs/FTO sensor. Reprinted with the permission from ref. [122]; **D)** Illustration of the fabrication process of MIP/GO/CdS/CS/ITO sensor by UV polymerization (using metacrylic acid, AIBN and EGDMA), and the mechanism of photocurrent generation at fumonisin B_1 detection. Reprinted with the permission from ref. [125].

Table 1: Applications of MIP-based PEC sensors

Photoactive material	**MIP**	**Analyte**	**Type of polymerization**	**LOD**	**Ref.**
MIP PPy@TiO_2 NTs	Polypyrrole	Bisphenol A	Electropolymerization	2 nM	[111]
ITO/SnO_2/MIP	Polypyrrole	Bisphenol A	Electropolymerization	1.2 nM	[112]
FTO/ZnO-NRs/MIP-PPy	Polypyrrole	Bisphenol S	Electropolymerization	0.7 μM	[39]
MIP/ZnO/Au-PWE	Polypyrrole	Pentachlorophenol	Electropolymerization	4 pg mL^{-1}	[113]
MIPPy/Sn_3O_4@CFP	Polypyrrole	2,4-dichlorophenoxyacetic acid	Electropolymerization	1.08×10^{-11} M	[115]
MIP/CdS-GR/FTO	Polypyrrole	4-aminophenol	Electropolymerization	2.3×10^{-8} mol L^{-1}	[114]
MIP-B-TiO_2 NRs	p-aminothiophenol	Chlorpyrifos	Electroplymerization	7.4 pg mL^{-1}	[117]
MIP-AuNPs/TiO_2 NTs	o-phenylenediamine	Chlorpyrifos	Electroplymerization	0.96 nmol L^{-1}	[116]
MIP/Bi_2S_3/ITO	o-phenylenediamine	Dioctyl phthalate	Electropolymerization	0.1 pM	[118]
MIP/$AgBiS_2$/Bi_2S_3/Ti	o-phenylenediamine	Propoxur	Electropolymerization	2.3×10^{-13} mol L^{-1}	[119]
MIP/AuNPs/μPAD	o-phenylenediamine	L-glutamic acid L-cysteine	Electropolymerization	9.6 pM 24 pM	[120]
MIP@TiO_2 NTAs	Acrylamide, EGDMA, AIBN	Perfluorooctane sulfonate	UV-polymerization	86 ng mL^{-1}	[121]
MIP@AgI-BiOINFs/FTO	Acrylamide, EGDMA, AIBN	Perfluorooctanoic acid	UV-polymerization	0.01 ng mL^{-1}	[122]
MIP/g-C_3N_4/FTO	4-vinylpyridine, EGDMA, AIBN	Bisphenol A	Thermal polymerization	1.3 μmol L^{-1}	[123]
MIP/GO/CdS/CS/ITO	Methacrylic acid, EGDMA, AIBN	Fumonisin B_1	UV-polymerization	4.7 pg mL^{-1}	[125]
MIP/CdS/Pdots/CS/ITO	Methacrylic acid, EGDMA, AIBN	α-Solanine	UV-polymerization	6.5 pg mL^{-1}	[126]
CdTe QDs@MIPs/Au-WE	CdTe QDs, acrylamide, EGDMA, AIBN	S-fenvalerate	Thermal polymerization	3.2×10^{-9} mol L^{-1}	[128]
MIT/CA	TiO_2	Atrazine	Chemical polymerization	0.008 μM	[110]

Abbreviations: AIBN – 2,2-azobisisobutyronitrile, Au-WE – gold working electrode, AuNPs – gold nanoparticles, CA – carbon aerogel, CFP – carbon fiber paper, CS – chitosan, EGDMA – ethylene glycol dimethacrylate, FTO – fluorine doped tin oxide, g-C_3N_4 – graphitic carbon nitride, GO – graphene oxide, GR – graphene, ITO – indium tin oxide, MIP – molecularly imprinted polymers, MIT – molecular imprinting technique, μPAD – microfluidic paper-based analytical device, NFs – nanoflakes, NRs – nanorods, NTAs – nanotube arrays, NTs – nanotubes, Pdots – polymer dots, PPy – polypyrrole, PWE – paper working electrode, QDs – quantum dots



Graphical abstract