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Chitosan/Gold Nanoparticles Nanocomposite Film for Bisphenol A Electrochemical Sensing

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Abstract: Bisphenol A (BPA) is considered an endocrine-disrupting compound and can cause toxicological effects, even at low doses. The development of sensitive and reliable sensors that would allow the detection of such contaminant is highly pursued. Herein, we report an electrochemical sensing strategy based on a simple and low-cost nanocomposite film sensor platform for BPA detection. The platform was developed by modifying a fluorine-doped tin oxide (FTO) electrode with layer-by-layer (LbL) films of chitosan (Chi) and gold nanoparticles functionalized with a polythiophene derivative (AuNPs:PTS). The growth of the Chi/AuNPs:PTS LbL films was monitored by UV–Vis spectroscopy. Electrochemical characterization revealed that the three-bilayer film exhibited the highest electrocatalytic performance and differential-pulse voltammetry (DPV) measurements demonstrated that the modified electrode was suitable for BPA detection through a quasi-reversible and adsorption-controlled electrochemical oxidation and reduction process. The developed sensor exhibited a linear response range from 0.4 to 20 μmol L^{-1}, with a detection limit of 0.32 μmol L^{-1}. The sensor showed good reproducibility with relative standard deviations of 2.12% and 3.73% to intra- and inter-electrode, respectively. Furthermore, the platform demonstrated to be suitable to detect BPA in real water samples, as well as selective for BPA detection in solutions with 100-fold excess of common interfering compounds.

Keywords: bisphenol A; chitosan; gold nanoparticles; layer-by-layer; electrochemical detection

1. Introduction

Bisphenol A (BPA; 2,2-bis(4-hydroxyphenyl) propane) is an endocrine disruptor compound widely employed as an intermediate in the production of polycarbonate plastics and epoxy resins, which are widely used for food packaging [1]. Several studies have reported that BPA is capable to disrupt many metabolic pathways, even at low concentrations (traces), leading to substantial damage to tissues and organs [2–4]. In this regard, efforts have been made to spread the awareness message of products containing BPA. For instance, plastics labelled with recycle codes 3 or 7 are more likely to contain BPA [5]. Moreover, its widespread use has led to environmental pollution. In view of its increasing harmful impact to the environment and human health, there is an urgent need to develop a more convenient and reliable method to analyze BPA in various matrices. In this regard, different approaches have been reported and explored to detect and quantify BPA [6–9]. Among

them, electrochemical techniques stand out due to their merits of simple operation, short analysis time, low cost and high sensitivity [10–12].

In recent years, the working electrode modification with nanomaterials has become an efficient approach to enhance the surface area of an electrode for improved electrochemical-sensing performance [13–15]. Moreover, the use of conductive nanomaterials, such as metallic nanoparticles, conducting polymers and carbon-based nanomaterials, can also enhance electron transfer during the catalytic reaction [14]. Therefore, the choice of nano-material and its deposition technique are key in determining the sensing performance. In this regard, layer-by-layer (LbL) assembly appears as a simple, low-cost and versatile technique for the design of sensors using self-assembled functional nanomaterials with their composition and structure controlled at nanoscale [16].

With this in mind, herein, we report on the design, characterization and application of a sensor platform based on LbL film for the selective electrochemical detection of BPA. Multilayer films were fabricated using chitosan (Chi) as polycationic material and gold nanoparticles (AuNPs) stabilized with polythiophene sulfonate poly[2-(3-thienyl) ethyloxy-4-butylsulfonate] sodium salt (AuNPs:PTS) as polyanionic material. Chi and AuNPs:PTS were combined to build the nanostructured electrode due to their film-forming ability and good conductivity, respectively. The wide linear range and detection limit of FTO electrode modified with Chi/AuNPs:PTS LbL films were characterized by the differential-pulse voltammetry (DPV) technique. This sensor was further used to detect BPA in a real water sample.

2. Materials and Methods

2.1. Materials

All reagents used were of analytical grade and used as received. Bisphenol A (BPA, ≥99%), Cathecol (≥99%), Hydroquinone (≥99%), Phenol (≥99%) and Chi with a medium molecular weight were purchased from Sigma-Aldrich (St. Louis, MO, USA). Glacial acetic acid, sodium acetate, hydrochloric acid (HCl ACS reagent, 37%), potassium hexacyano-ferrate (II) trihydrate (ACS reagent, 98–102.0%) and potassium chloride (ACS reagent, 99.0–100.5%) were obtained from Synth (São Paulo, Brazil). All aqueous solutions were prepared with ultrapure water (resistivity of 18 MΩ cm).

A BPA stock solution (1.0 mmol L^{-1}) was prepared in ethanol (Synth Chemical, São Paulo, Brazil). A 0.01 mol L^{-1} phosphate buffer (PBS) solution with pH 7.4 was used to dilute the solutions.

2.2. Synthesis of AuNPs:PTS Nanoparticles

Gold nanoparticles stabilized with polythiophene sulfonate poly[2-(3-thienyl) ethyloxy-4-butylsulfonate] sodium salt (AuNPs:PTS) were synthesized according to previous work [17]. Briefly, AuNPs were prepared by reducing gold (III) chloride ($HAuCl_4$) solution, with aqueous sodium citrate in the presence of PTS; both PTS and citrate help to stabilize the AuNPs. All details about the synthesis and characterization of AuNPs:PTS can be found in the reference [17].

2.3. Layer-by-Layer (LbL) Films' Fabrication and Characterization

A solution of 0.5 mg mL^{-1} of Chi was prepared by dissolving the polymer in acetic acid aqueous solution (1%). AuNPs:PTS solution was used as prepared. The Chi/AuNPs:PTS LbL films were deposited on conventional glass and FTO glass substrates (1.5 cm × 0.5 cm) by alternating immersion into cationic (Chi) and anionic (AuNPs:PTS) solutions for 10 min and 1 h, respectively. The adsorption time used for both materials was chosen according to previous results [17,18]. The functional area of the designed electrode (area functionalized with LbL films) was limited in 0.25 cm^2. UV-Vis absorption spectroscopy analysis (Jasco—V-730) was used to monitor the growth of the films and cyclic voltammetry measurements was used to characterize its electron transference properties.

2.4. Electrochemical Measurements

All electrochemical measurements were carried out using a PGSTAT204 Autolab (Metrohm) electrochemical system, controlled by a NOVA (version 2.1.4, Metrohm Autolab BV, Utrecht, Netherlands) software. The FTO-Chi/AuNPs:PTS electrodes were placed as working electrodes. The counter and reference electrodes were a Pt foil and Ag/AgCl (3 mol L^{-1} KCl), respectively. The experiments were carried out by cyclic voltammetry (CV) and DPV using PBS solution (0.01 mol L^{-1}, pH 7.4) at room temperature. For electrochemical characterization of LbL films, the CV analysis was performed using a solution of 0.05 mol L^{-1} [Fe(CN)$_6$]$^{3-/4-}$ with 0.1 mol L^{-1} KCl, varying the potential from −0.5 to 1.0 at 0.1 V s^{-1}. For oxidation mechanism study, CVs were performed using 1 μmol L^{-1} of BPA in buffer solution (pH 7.4) varying the scan rate from 5 to 300 V s^{-1} over a potential range from −0.3 to 0.8 V. The DPV analysis was carried out in the potential range from 0.0 to 0.7 V using a pulse amplitude of 25 mV, a step potential of 5 mV at a scan rate of 10 mV s^{-1}.

3. Results and Discussion

3.1. Choice of Materials

It has been proven that the choice of materials to design sensing platforms directly influences the sensing performance. Chi, a cationic polysaccharide with abundant amines, has attractive properties including excellent film-forming ability and adhesion. The AuNPs:PTS, at a ratio of 1:1, was chosen based on its better charge transfer ability (compared with other synthesized proportions) showed by impedance measurements in our previous work [17]. PTS acts as stabilizing agent for the AuNPs and helps the LbL film formation, once its sulfate groups negatively charged can interact with the amine positively charged from chitosan by electrostatic interactions. Therefore, it is expected that this film architecture presents adhesion on the working electrode and promotes a great transfer electron transfer between the electrode/solution interface, allowing the BPA detection as shown in Scheme 1.
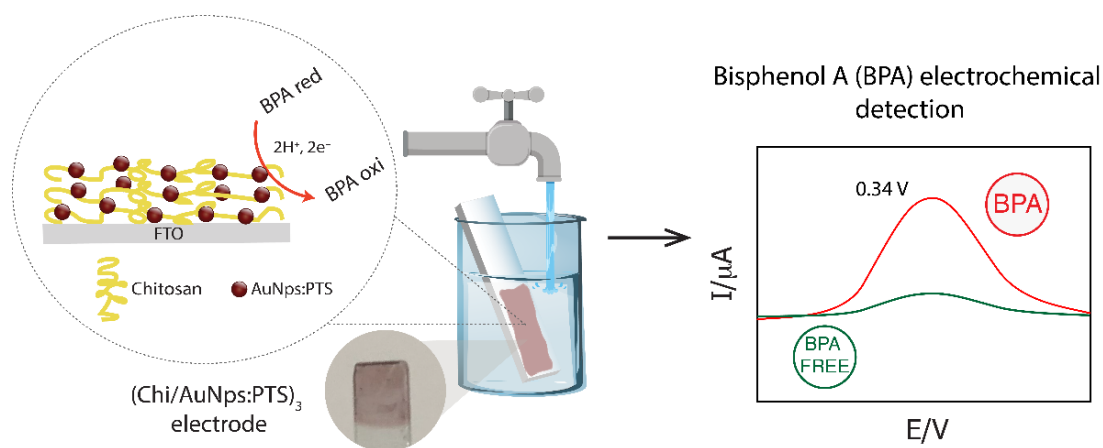
Scheme 1. Schematic representation of the electrochemical detection of BPA at Chi/AuNPs:PTS electrode interface.

3.2. Characterization of Chi/AuNPs:PTS LbL Films

The sequential growth of the Chi/AuNPs:PTS LbL films was monitored by UV-Vis absorption spectroscopy, as shown in Figure 1a. The spectra show an absorption band centered at 537 nm assigned to the AuNPs surface plasmon resonance [17,19]. As chitosan does not exhibit any UV-Vis absorption, the band related to nanoparticles was used to monitor the film formation. A linear growth was observed for films from one to five bilayers, which suggests that the same amount of material (Chi/AuNPs) was adsorbed in the substrate in each bilayer. Figure 1b shows the cyclic voltammograms performed in [Fe(CN)$_6$]$^{3-/4-}$ solution for all films, with a quasi-reversible one-electron redox behavior ($I_{pa}/I_{pc} \sim 1$) [20]. All modified electrodes showed an increased peak current compared

to the bare electrode, suggesting a good electron-mediating property of the LbL films. The highest increase in the anodic (I_{pa}) and cathodic peak current (I_{pc}) was observed for the (Chi/AuNPs:PTS)$_3$. Compared to bare FTO, the increase was from 2352 µA to 2889 µA to I_{pa} and from 2206 µA to 2613 µA to I_{pc}. The inset in Figure 1b highlights its increment and confirms the faster electron transfer kinetics promoted for the electrode modified with three bilayers. Based on this, the (Chi/AuNPs:PTS)$_3$ electrode was chosen as a platform for BPA detection.
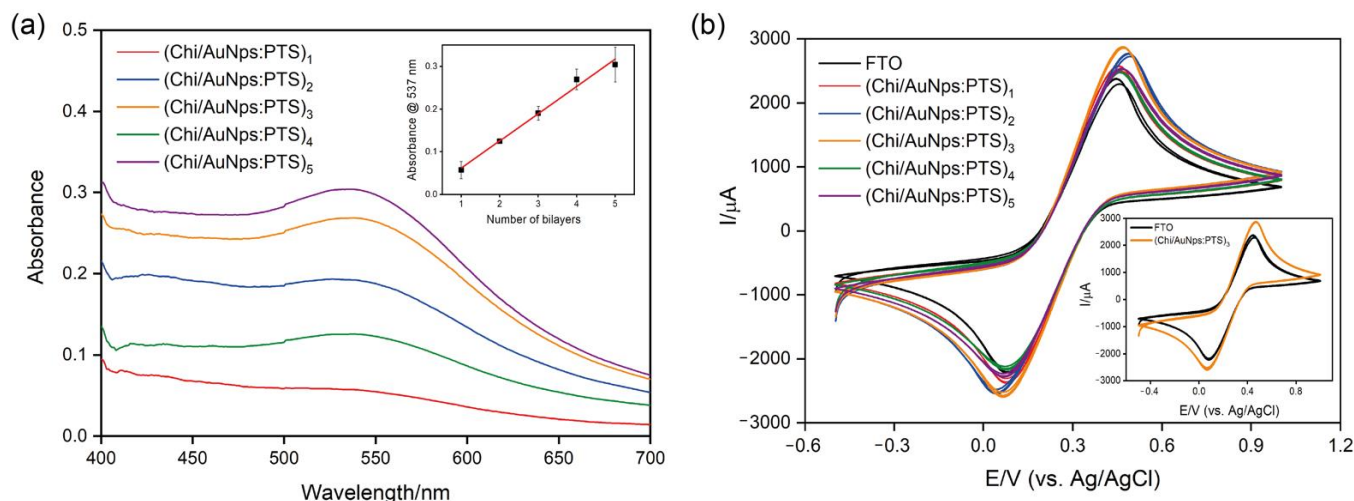

Figure 1. (**a**) UV–vis absorption spectra (from 400 to 700 nm) for LbL films ranging from 1 up to 5 bilayers of Chi/AuNPs:PTS. Inset shows the dependence of the absorbance with the number of deposited bilayers. (**b**) Cyclic voltammograms for FTO and FTO-(Chi/AuNPs:PTS) LbL films in 5 mmol L^{-1} [Fe (CN)$_6$]$^{3-/4-}$ solution with 0.1 mol L^{-1} KCl. The inset highlights the comparison between the CVs obtained for bare FTO and FTO-(Chi/AuNPs:PTS)$_3$ bilayers.

The role of scan rates on the CV curves was investigated in order to provide insights about BPA electrochemical behavior on the designed electrode surface. Figure 2a shows the response for scan rates from 20 mV s^{-1} to 300 mV s^{-1} recorded in 3 µmol L^{-1} of BPA. The redox peaks were observed centered at 0.49 and 0.35 V and are related to the BPA oxidation (anodic peak) and reduction (cathodic peak) process, respectively [21]. As can be noticed in Figure 2a, the anodic and cathodic peak currents increased with the increase in the scan rate from 5 to 300 mV s^{-1}. Moreover, Figure 2b displays that both I_{pa} and I_{pc} increased linearly with the scan rate. Such a linear increase indicates that the electrochemical reaction of BPA at the FTO-(Chi/AuNPs:PTS)$_3$ interface is an adsorption-controlled process [19,22].

The oxidation process of BPA at the as-prepared electrode surface shows a quasi-reversible behavior, observed for the cathodic and anodic peaks potential separation which suggests a quasi-reversible process [20,22]. According to these results, the proposed mechanism for BPA electrooxidation at the interface of the (Chi/AuNPs:PTS)$_3$ electrode consists of the transfer of two electrons and two protons [23], as depicted in Scheme 2.

DPV was employed to verify the (Chi/AuNPs:PTS)$_3$ electrode efficiency in detecting BPA. DPV is an excellent method for sensing, with advantages such as high sensitivity and low LOD, being extremely useful for measuring trace levels of analytes [24]. As shown in Figure 3, the oxidation peak current centered at approximately 340 mV increases upon addition of different BPA concentrations. The anodic peak current variation with the log of BPA concentration shows a linear region following the equation: Ip (µA) = 1.22 × 10^{-8} [log [BPA](µM)] + 2.40 × 10^{-7} (R^2 = 0.99), yielding a linear concentration range from 0.4 to 20 µmol L^{-1}, as displayed in the inset of Figure 3. An LOD of 0.32 µmol L^{-1}, was calculated using the equation Y= blank + 3 SD (where SD is the standard deviation).
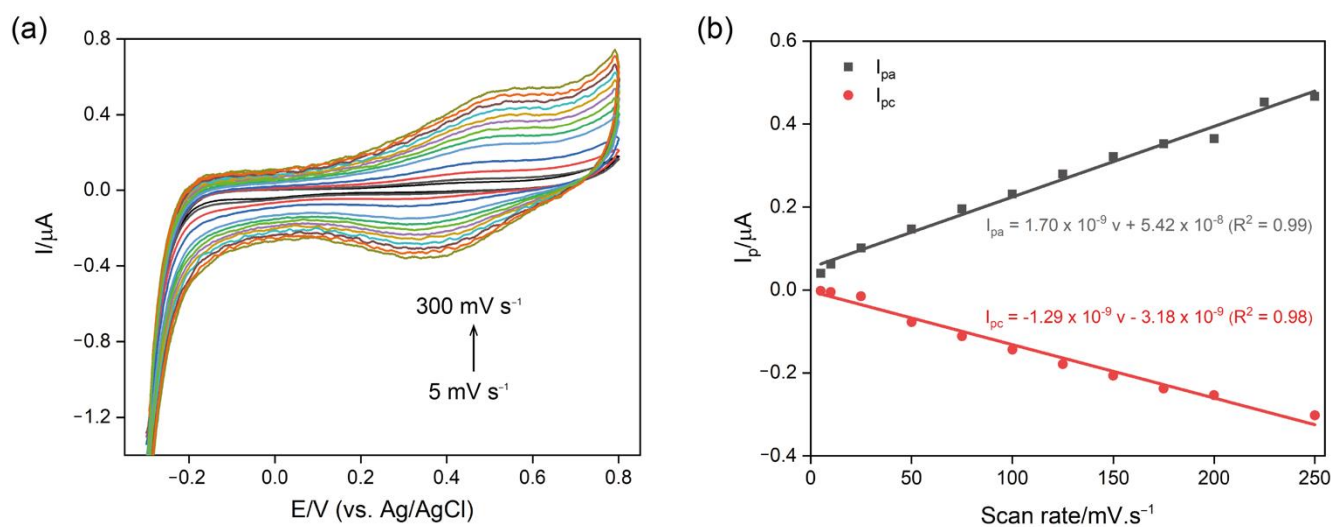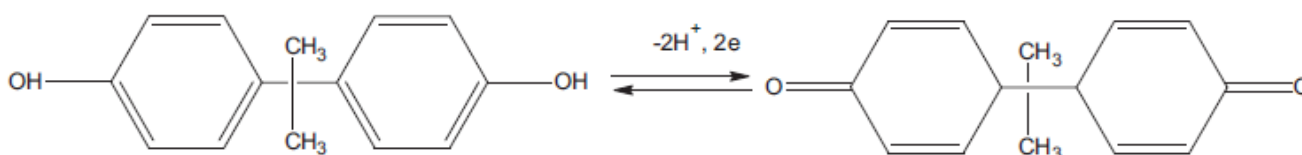
Figure 2. (**a**) Voltammograms for 1 μmol L^{-1} BPA in 0.01 mol L^{-1} PBS solutions (pH 7.4) at different scan rates, ranging from 5 to 300 mV s^{-1} using the FTO-(Chi/AuNPs)$_3$. (**b**) Dependence of the oxidation and reduction peak current (I_p) with the scan rate.

Scheme 2. Proposed reaction mechanism for the BPA electrochemical oxidation at the (Chi/AuNPs:PTS)$_3$ electrode interface.
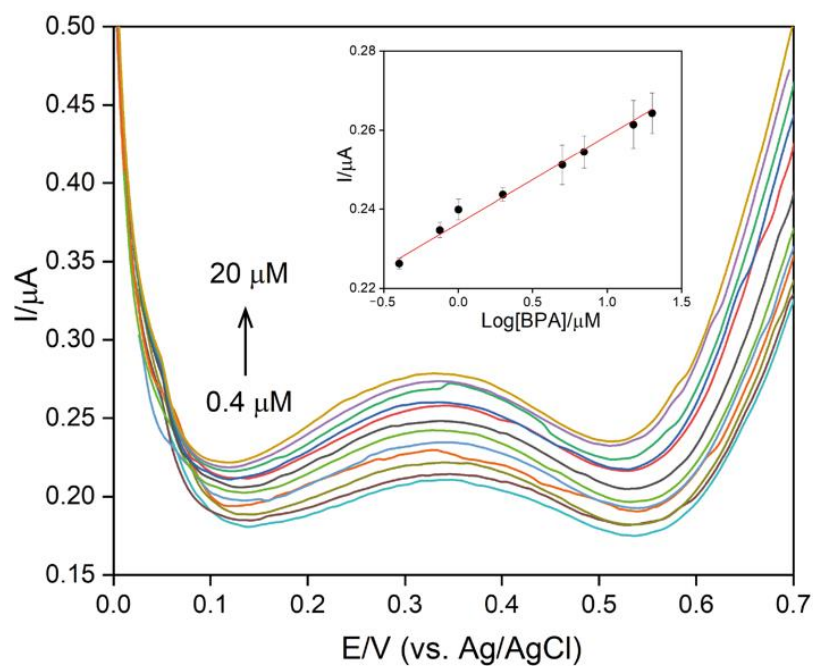

Figure 3. DPV curves at different concentrations of BPA for FTO-(Chi/CNTs)$_3$ in 0.01 mol L^{-1} PBS (pH 7.4). The inset shows the linear relationship between the peak current (I_p) and log of BPA concentrations.

The (Chi/AuNPs:PTS)$_3$ electrode selective response to BPA was verified by carrying out interference studies. The performance was evaluated in the presence of other phenolic compounds. The results showed that 100-fold excess of the 4-nitrophenol, catechol, phenol and hydroquinone caused approximately 15%, 0.2%, 7% and 27% of variation, respectively, in the response current peak, as displayed in Figure 4. Except for hydroquinone, the low values found for 4-nitrophenol, catechol, and phenol indicate no significant interference, showing that these chemical species did not affect the determination of BPA using the (Chi/AuNPs:PTS)$_3$ electrode.
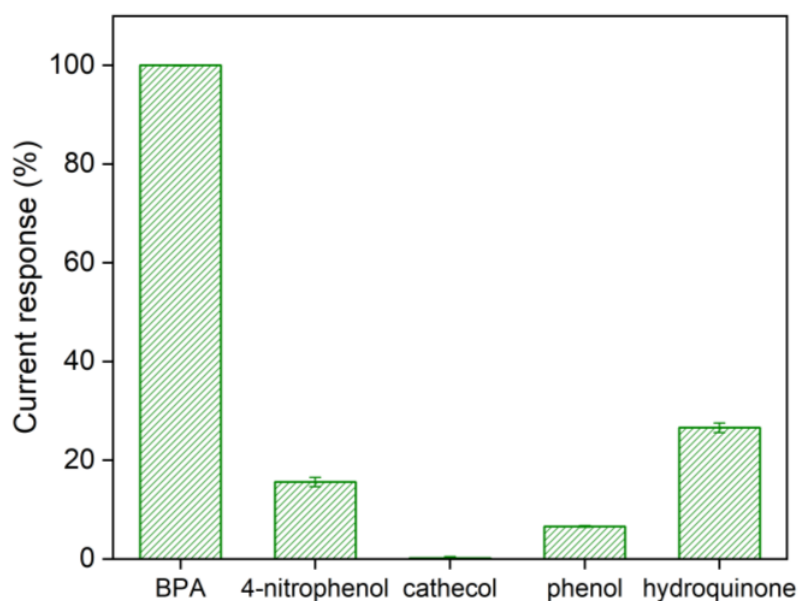

Figure 4. Relative current percentage upon several possible interferents for evaluating the sensor selectivity.

The electrode repeatability and reproducibility were also investigated by performing repeated voltammetry experiments with solutions containing 1 μmol L^{-1} of BPA. Ten successive measurements on the single modified electrode yielded a reproducible current with a relative standard deviation (RSD) of 2.12%. Additionally, the DPV responses of three similarly prepared electrodes were evaluated and the obtained RSD value was 3.73%, confirming the robustness of the modification procedure.

In order to evaluate the performance of (Chi/AuNPs:PTS)$_3$ in practical analytical applications, the determination of BPA in real samples of tap water was carried out using the recovery analytical procedure. The water samples, without pretreatment, were spiked with 5 and 10 μmol L^{-1} of BPA and the percentage of recoveries was found to be 92 and 102%, respectively, indicating that the sensor might be sufficient for practical applications of tap water.

Compared with other electrochemical BPA sensors (Table 1), the proposed sensor presented a broad linear range and a relatively low LOD. Its competitive performance compared to other sensing platforms may be ascribed to the synergistic effect between the AuNPs and chitosan. Moreover, it could be stated that our strategy for developing an electrochemical sensor for BPA detection has properties of low cost, ease of preparation, robustness, and could be used, for instance, for the fabrication of flexible and disposable electrodes, allowing its practical use.

Table 1. Comparison of the analytical performance of the proposed sensor with other AuNPs-modified electrode sensors for BPA determination.

Electrode	Electroanalytical Method	Detection Limit ($\mu mol\ L^{-1}$)	Linear Range ($\mu mol\ L^{-1}$)	Ref.
MWCNTs [a]/AuNP/Paper	LSV	0.131	0.876–87.6	[25]
AuPdNPs/GNs [b]	DPV	0.008	0.05–10	[26]
AuNps-GR [c]/GCE	DPV	0.005	0.01–10	[27]
AuNps/SGNF [d]/GCE	LSV	0.035	0.08 to 250	[28]
Fe_3O_4 NPs-Si$_4$Pic$^+$Cl$^-$ [e]/AuNps-Si$_4$Pic$^+$Cl$^-$/GCE	DPV	0.007	0.02 to 1.4	[29]
AuNP/MWCNT/GCE	DPV	0.004	0.01 to 0.7	[30]
La^{3+}/ZnO NFs/GSPE	DPV	0.25	0.8 to 300.0	[31]
Flexible SPE [f] electrochemically treated with H_2SO_4	DPV	0.95	2-50	[32]
(Chi/AuNPs:PTS)$_3$	DPV	0.32	0.4 to 20	This work

[a] MWCNTs: Multi-walled carbon nanotubes; [b] GNs: graphene nanosheets; [c] GR: dotted graphene; [d] SGNF: stacked graphene nanofibers; [e] Si$_4$Pic$^+$Cl$^-$: polymer solution of 3-n-propyl-4-picolinium silsesquioxane chloride; [f] SPEs: screen-printed carbon electrode.

4. Conclusions

We developed a simple, cheap, and suitable platform for BPA electrochemical sensing using FTO electrode modified with LbL film architectures of chitosan and AuNPs@PTS. CV measurements revealed that the modified electrode exhibited a quasi-reversible behavior at the BPA. The oxidation and reduction process via the two-proton/two-electron process were found to be adsorption-controlled. The as-prepared electrode displayed a good LOD of 0.32 $\mu mol\ L^{-1}$ and good reproducibility. Moreover, no significant interference was found for 100-fold excess of 4-nitrophenol, catechol and phenol in the determination of target analyte. The recovery test showed that the designed electrode can be successfully applied in the detection of BPA in a real water sample. Furthermore, the electrode modification procedure reported here is simple, low-cost, not time-consuming and results in a robust sensor, thereby offering potential for preparation of commercial modified electrodes.

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Conflicts of Interest: The authors declare no conflict of interest.

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