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Review

Recent Advances in Electrochemical Sensing of Isoproterenol

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One of the sympathomimetic beta-adrenergic agonist medications is isoproterenol (IP), which is utilized for the treatment of heart block or bradycardia. It applies positive chrono-tropic and inotropic impacts on heart in case of heart attack, bronchitis, and cardiac chock. However, its excessive dosage may result in the arrhythmias or heart failure. Consequently, it is necessary to devise simplistic, fast, and affordable assays (e.g., electro-chemical determination) for aiding the clinical diagnostic and treatments of IP. In this review, we have covered important techniques and electrode substances utilized for the IP analysis base on the nanostructured electrodes and their chemically modifications. In addition, we have illustrated the advantages and disadvantages of the presented the electrode materials for the IP analyses.

Keywords: Isoproterenol, drug, Clinical diagnostics, Electrochemical detection, Chemically modified Electrodes.

1. INTRODUCTION

Determination of medicine species contributes importantly to the control of the drugs quality and greatly influences on the public health [1]. Hence, it is very critical to propose novel approaches to construct analytical instruments for accurately determining the medicines at the trace levels [2]. IP or 4-

[1- hydroxy-2-(propan-2-ylamino) ethyl] benzene-1, 2-diol is one of the synthetic catecholamines which is considered as one of the nonselective β-agonists [3,4]. Myocardial damages in the sub-endocardial layer of the left ventricle are induced by administrating IP, which shows acute extensive myo-fibrillar degeneration [5-7]. Therefore, a single sub-cutaneous injection of IP (85 mg kg^{-1}) may generate fibrosis and myo-cardial necrosis in the rats, and iterated injection might enhance the scope of myocardial injuries [8-11]. According to the metabolomic pathway analyses, IP has a negative impact on the energy metabolism because of abnormal metabolism of hypo-taurine, taurine, glycine, arachidonic acid, threonine, histidine, and serine disturbs optimum citrate cycle and tricarboxylic acid and enhancement of glycolysis [12-16]. Moreover, outputs verified considerable modifications after myocardial damages that involve calcium over-load, deficiency of energy metabolism and inflammation in their patho-physiological procedures. This drug is utilized for heart block and bradycardia. In fact, via the activation of 1-receptors on heart, positive dromotropic, inotropic and chronotropic impacts would be induced by the drug [17,18]. In fact, IP applies positive chronotropic and inotropic impacts on heart. In addition, it results in vasodilatation in the skeletal muscle arterioles and its chrono-tropic and inotropic impacts raise the systolic blood pressure (SBP) whereas its vasodilatory impact lowers diastolic blood pressure (DBP). In fact, the medicine is consumed in bronchitis, heart attack, and cardiac chock. Nonetheless, excessive material may lead to arrhythmias and causes heart failure [19,20]. Hence, determining this compound is of high importance. Therefore, a variety of techniques like chemiluminescence [24], chromatography [21-23], capillary electrophoresis [26] and spectrophotometry [25] have been employed to determine IP. Nonetheless, the techniques have a number of caveats like expensiveness, laborious operations, inappropriateness for on-site analyses, and necessity for the expert operators as well as complex equipment. Thus, it is of high importance to devise other determination methods to detect IP.

It should be noted that electro-chemical procedures have generally been considered to be appropriate for ordinary analyses of IP. The techniques decline expenses and facilitate the procedure due to the easiness with which the electro-chemical devices may be operated. Experts in the field devised a lot of electro-chemical techniques to detect IP in various specimens. For this reason, electro-chemical analyses of IP are cheap, simplified, sensitive, and rapid and thus could be implemented with the portable miniaturized instruments. In fact, a working electrode should be obtained to fulfill desirable features for routine analyses in the laboratories verified by the experts in the field. Therefore, the present review overviews the currently published electrode substances and techniques to electrochemically analyze IP. Hence, it has a particular focus on the current studies in this area, especially investigations conducted since 2000. Consequently, numerous instances of the electrode substances and the most significant features of the previous techniques may be readily observed. Finally, this review presents various working electrode substances utilized in electro-chemical IP analysis.

2. ELECTROCHEMICAL SENSING BY THE MODIFIED ELECTRODES

It is well-known that electro-chemical sensors are usually based on the redox reaction, including target analyte in electrolyte at a working electrode that changes the electrical signal. However, the produced signal is proportionate with the analyte concentration. Experts in the field measured electrical

signal and categorized electro-chemical processes into the impedimetric, conductometric, voltammetric, amperometric, and potentiometric procedures [27]. Among them, voltammetric techniques have been further investigated. In fact, a Czech scientist Jaroslav Heyrovsky identified voltammetry in 1920s. Voltammetric procedures utilized the measuring current as a function of voltage in the current-voltage curve. Over the past years, researchers viewed these techniques, including differential pulse voltammetry (DPV), square-wave voltammetry (SWV), linear sweep voltammetry (LSV), cyclic voltammetry (CV), and so on as one of the popular devices for determining trace concentration of prominent compounds as a result of its increased sensitivity and accuracy.

Researchers exhibited an ever-increasing interest in the electro-chemical sensors for drug, food, environmental and agricultural analysis because of the electro-chemical behaviors of bio-molecules and medicines and partially as a result of the advancements in the electro-chemical measuring systems [28-32]. On the one hand, a combination of rapid, selective, sensitive, miniaturized, affordable and accurate electro-chemistry based sensing and areas such as bio-chemistry, proteomics, nanotechnology, drug and molecular biology analyses resulted in the development of the electro-chemical sensors [33-36]. One of the significant solutions for ameliorating the electrode functions is to add a chemical modifier or functionalizing the material base of the electro-chemical sensors. Therefore, chemical modification of the inert substrate electrode with the modifiers would be accompanied by major benefits in designing and developing the electro-chemical sensors. During the operation, redox active sites would frequently shuttle the electrons between the analyte solution and substrate electrodes while significantly reducing the activation over-potential. Another benefit of the chemically modified electrodes has been proposed to be their lower susceptibility to the surface fouling and oxide formation in comparison with the inert substrate electrodes [37-44].

3. MODIFYING CARBON PASTE ELECTRODE (CPE) TO DETERMINE IP

Carbon has been considered as one of the desirable electrode substrates because of its broad anodic potential range, lower residual current, chemical inertness, simplistic utilization, and affordability. In addition, carbon exhibits rapid response duration and may be built in various sizes. During the last years, carbon paste; that is, a mix of a binder (pasting liquid) and carbon (graphite) powder has become one of the commonest carbon electrodes utilized for laboratory procurement of diverse sensors, detectors and electrodes. There is no doubt that this condition results from the optimized constellation of physico-chemical as well as electro-chemical features of this carbon such as substrate that achieved the increased popularity amongst practical and theoretical electro-chemists and beyond boundaries of the electro-chemical sciences. In fact, CPEs provided benefits, including lower background current, simplified construction, affordability, as well as renewable surfaces [45-48]. However, they show higher over-potentials in numerous analytes. Moreover, the bare CPEs do not extensive utilizations in the direct electro-analysis [49] and thus multiple investigations have emphasized their chemical modification that is one of the procedures wherein surface or balk materials of the electrodes are chemically altered.

4. MODIFYING CPE WITH GRAPHITE (Gr) AND GRAPHENE OXIDE (GO)

Graphite has been considered to be one of the flat monolayers of carbon atoms strongly packaged into a two-dimensional (2D) honey-comb lattice. Gr has acceptable electrical conductivity, higher electro-catalytic activities, higher surface areas and stronger mechanical strength [50,51]. Moreover, excellent electronic features of Gr indicated its capability for promoting electron transfer in case of utilization as the electrode material, providing a novel solution for designing new electro-chemical bio-sensors and sensors [52-57]. Therefore, the modified Gr electrodes showed substantial application for studying or determining a number of organic and some biological molecules [58-62].

In addition, synthesis of a ferrocene-derivative compound, 1-(4-bromobenzyl)-4-ferrocenyl-1H-[1,2,3]-triazole (1,4-BBFT) has been performed and utilized for constructing a modified graphene paste electrode (GPE) (Tajik et al.). Moreover, hydrophilic ionic liquid (IL) (n-hexyl-3-methyl-imidazolium hexa-fluoro phosphate) has been applied as the binder for procuring the modified electrode. IP electro-oxidation at the modified electrode surface has been investigated with CV, SWV and chrono-amperometry (CA). At optimum condition, SWV peak current of IP showed linear enhancement with IP concentration ranging between 6.0×10^{-8} and 7.0×10^{-4} M and limit of detection (LOD) equal to 12.0 nM for IP. Furthermore, diffusion coefficient ($D = 9.54\times10^{-6}cm^2/s$) and kinetic variables like electron transfer coefficient ($\alpha = 0.4$) and heterogeneous rate constant ($k = 2.5\times10^{3}\ mol^{-1}Ls^{-1}$) to oxidize IP oxidation have been detected. The procured modified electrode displayed an excellent resolution between voltammetric peaks of IP, theophylline and acetaminophen that made it appropriate to determine IP in the presence of theophylline and acetaminophen in the real specimens [63].

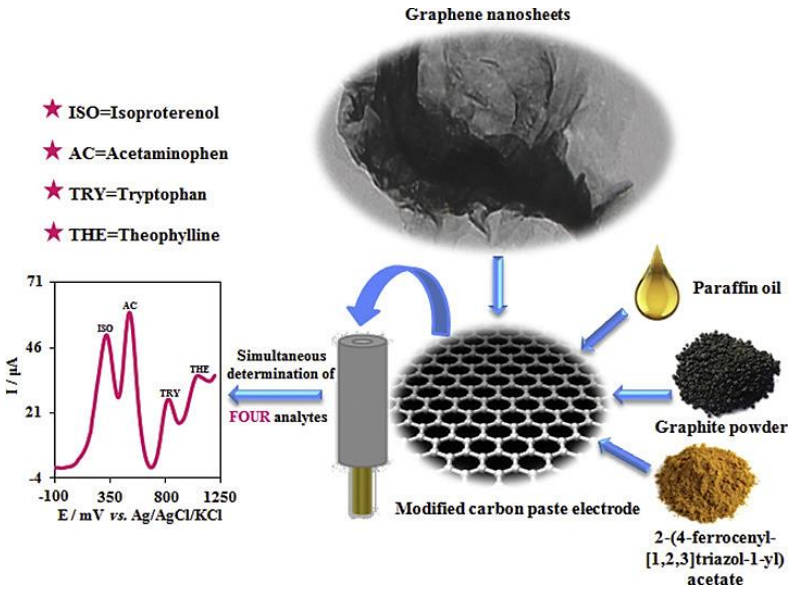

Figure 1. A simplified technique for the simultaneous determination of IP, tryptophan, theophylline, and acetaminophen. Reused with permission from Ref. [63] Copyright 2017 Elsevier.

Beitollahi et al. devised a selective and sensitive electro-chemical CPE modified with ethyl 2-(4-ferrocenyl-[1,2,3] triazol-1-yl) acetate (EFTA) (EFTAG-CPE) and Gr for simultaneously determining

IP, tryptophan, theophylline and acetaminophen (Figure 1). It has been demonstrated that electrode has major electro-catalytic activity in oxidation of various analytes in the phosphate buffer solution (PBS) (pH of 7.0) and shows well-resolved oxidation peak with considerable difference; that is, 0.190 V between acetaminophen and IP, 0.510 V between tryptophan and IP, and 0.750 V between theophylline and IP. Therefore, IP electro-chemical reaction has been examined with the use of electrodes in CV and SWV. According to the outputs, the reaction has been highly simplified as shown by the augmented oxidation current and shifting oxidation potential to a less positive potential against the case of the bare CPEs. Furthermore, oxidation current had a direct proportionate with IP concentration in a range from 0.1 to 40.0 and 40.0 to 600.0 μM and LOD (3ϭ) equal to 0.034 μM (S/N = 3) has been seen for this analyte via the SWV analysis on the basis of EFTAGCPE. Finally, electrode could be utilized in the real specimens [63].

Based on Mazloum Ardakani et al.'s investigation, electro-chemical features of a CPE modified by the synthesized carbon nanoparticles (NPs), new derivative of hydroquinone, reduced graphene oxide (RGO), (Z)-4-(naphthalen-1-yliminomethyl) benzene-1, 2-diol (NYB) have been examined using the CV. Therefore, they utilized modified electrode as one of the electro-chemical sensors for IP catalytic oxidation, which showed a very good electro-catalytic activity for IP with a reasonable electro-chemical function, higher conductivity and lower over-potential. Based on the optimized condition (pH of 7.0) in CV, IP oxidation potential declined to approximately 324 mV at the modified electrode in comparison with the un-modified CPE. In addition, DPV displayed 2 linear dynamic ranges between 0.5 and 80.0 μM and 80.0 and 1000.0 μM for IP. LOD for IP equaled 0.065 μM [64].

Mohammadi et al. also addressed synthesis of 3-(4'-amino-3'-hydroxy-biphenyl-4-yl)-acrylic acid (3,4'-AA) and utilized it for constructing a modified GO nano-sheet paste electrode (3,4'-AAGCPE). Moreover, IP electro-oxidation at the modified electrode surface has been examined with the use of CA, SWV as well as CV. They found that under optimum condition, SWV peak current of experienced linear enhancement with concentration of IP ranging between 2.5×10^{-8} and 2.0×10^{-5} M and LOD equal to 12 nM for IP. Ultimately, researchers utilized this modified electrode to detect IP in a number of real specimens [65].

Additionally, Rajabzadeh et al. illustrates developing RGO, Co (II) complex (cobalt (II) bis (benzoylacetone) ethylene-diimino) (CBE) modified CPE for IP simultaneous detection, carbon nanotubes (CNTs) tryptophan, and captopril. Furthermore, a pair of organized redox peak of Co (II) complex has been attained via a direct electron transfer between CPE and Co (II) complex. Their sensor exhibited highly effective electro-catalytic activities for IP anodic oxidation in a 0.1 M PBS at pH of 7.0. Furthermore, IP has been oxidized in the catalytic chemical reaction via the Co (III) produced through the electro-chemical reaction. Hence, in case of oxidation of Co (III) at a potential equal to182 mV, IP may be oxidized within this potential. Consequently, SWV had 2 linear dynamic ranges from 0.125-30.0 μM and 30.0-300.0 μM for IP. LOD for IP equaled 50 nM and their sensor has been satisfactorily employed for determining IP in real specimens like the human urine, IP ampoule and blood serum [66].

5. MODIFYING CPE WITH CNTs

According to the studies, CNTs have been proposed as a major nanomaterial as a result of their increased chemical stability, higher surface areas, higher mechanical features, specific electrical conductivity, mechanical strength, elasticity and metallic structural features [67-69]. In addition, experts in the field conducted notable attempts for fabricating various CNT morphology and exploring their utilization in diverse areas such as electro-chemical tools and sensors and composites [70-75].

In another study, Beitollahi et al. selectively determined IP in the presence of folic acid and uric acid with the use of 2,7-bis(ferrocenyl ethyl)fluoren-9-one modified CNT paste electrode (2,7-BFCNTPE) in 0.1 M PBS at pH of 7.0. They showed that the bare CPE would not separate IP voltammetric signals, folic acid, and uric acid. Nonetheless, 2,7-BFCNTPE resolved IP voltammetric signals, folic acid and uric acid with potential difference of 150 mV, 325 and 475 mV between uric acid-folic acid, IP-folic acid and IP-uric acid and remarkably augmented oxidation peak current of them in comparison with the bare CPE. In PBS at pH of 7.0, oxidation current showed a linear enhancement with 2 concentration intervals of IP so that one of them equaled 0.08 to 17.5 μM and the other equaled 17.50 to 700.0 μM. In addition, LOD (3σ) observed by DPV equaled 26.0 ± 2 nM. Moreover, functional utilization of the modified electrode has been displayed via detection of IP in, urine, human blood serum and IP injection [76].

The other investigation performed by Beitollahi et al. dealt with the electro-chemical sensor to determine IP. Their sensor has been on the basis of the CPE modified with 5-amino-2´,4´-di-methoxybiphenyl-2-ol (5ADMB) and used the CNTs. At the optimized pH equal to 7.0, IP oxidation occurred at a potential ~210 mV less positive than that of the un-modified CPE. According to the results, oxidation current showed a linear enhancement with 2 concentration intervals of IP so that one of them equaled 0.09 to 20.0 μM and the other equaled 20.0 to 400.0 μM. Furthermore, LOD (3σ) observed by SWV equaled 39.0 nM. Finally, functional utilization of the modified electrode has been shown via IP determination in urine, human blood and IP ampoule, serum specimens [77].

Again, Beitollahi et al. addressed the design, electro-chemical description, and usage of a new modified molybdenum (VI) complex-CNTPE for IP electro-catalytic detection. Therefore, they examined electro-chemical profile of this modified electrode using CV, which indicated a shift in oxidation peak potential of IP at 175 mV to less positive value in comparison to the un-modified CPE. In addition, researchers used DPV in 0.1 M PBS at a pH of 7.0 for determining IP in ranges between 0.7 and 600.0 μM and the LOD equaled 35.0 nM. Finally, the modified electrode has been utilized for determining IP in excessive folic acid and uric acid by DPV [78].

Beitollahi et al. focused on the construction of a CPE modified with 5-amino-3´, 4´-dimethylbiphenyl-2-ol (5ADB) and CNT. Their electrode modification targeted novel electro-chemical functions to detect IP in the presence of N-acetylcysteine and acetaminophen. Therefore, researchers registered peak potential in a PBS at the pH equal to 7.0, which has been 265 mV vs. Ag/AgCl/KCl (3.0 M) for IP. At the optimized pH of 7.0, IP oxidation happened at a potential around 215 mV less positive than that of the un-modified CPE. Finally, responses of the catalytic current with IP concentration indicated a linear correlation in ranges between 4.0×10^{-7} and 9.0×10^{-4}M with the LOD equal to 2.0×10^{-7} M [79].

In addition, Ensafi and Karimi-Maleh utilized the multi-wall carbon nano-tubes (MWCNTs) and the room temperature IL (i.e. 1-butyl-3-methylimidazolium hexafluoro phosphate and devised an electro-chemical procedure to detect IP. Researchers observed the oxidation peak potential in CV method of IP on the modified electrode to be 470 mV *versus* Ag/AgCl (at pH 6.0), whereas this peak potential at CPE occurred on about 605 mV at a similar scan rate equal to 100 mV s^{-1}. At the optimum condition, peak current has been linear to the IP concentration within a concentration range between 1.0 to 520 µM with the use of DPV. Moreover, LOD equaled 0.85 µM and their technique showed a satisfactory utilization to detect IP in urine specimens and ampoule [80].

Moreover, ferro-cenemonocarboxylic acid (FMA) modified CNTPE (FMA-CNTPE) has been fabricated in Ensafi et al. investigation. Researchers utilized it to determine IP at the trace levels. Therefore, the double step CA, electro-chemical impedance spectroscopy (EIS) and direct current CV demonstrated the capability of the modified electrode of catalyzing IP oxidation in the aqueous solution. Consequently, the kinetic variables of the system like the electron transfer coefficient (α=0.71) as well as the rate constant for chemical reaction (k_h =4.85×10^3 $M^{-1}s^{-1}$) between redox sites in FMA-CNTPE and IP has been specified with the use of the electro-chemical strategies. They applied DPV for quantitative analyses, which exhibited a linear dynamic range between 0.5 and 50.0 µM IP with the LOD equal to 0.2 µM IP. Furthermore, relative standard deviation (RSD%) for 10 subsequent assays of 5.0 µM IP equaled 1.9%. It is notable that their procedure has been explored as one of the selective, simplistic, and exact electro-chemical sensors to detect IP in the real specimens like urine and medicine [81]. In this study, Ensafi et al. also illustrated the electro-chemical procedure to voltammetrically detect IP in the presence of uric acid with the use of p-chloranil-CNTPE. Therefore, they applied CA, EIS and CV for investigating appropriateness of p-chloranil as a mediator for IP electro-catalytic oxidation at a pH of 10.5. Analysis showed linear enhancement of electro-catalytic current with the IP concentration on the concentration ranges between 0.015 and 100 µM and LOD for IP equaled 0.009 µM. Moreover, electro-chemical techniques have been used to determine diffusion coefficient and kinetics variables like the electron transfer coefficient and heterogeneous rate constant for IP. Finally, their technique showed successful application for IP detection in the urine and ampoule specimens [82].

Keyvanfard and Alizad have been among those who procured a sensor on the basis of a pyrogallol red modified MWCNT paste electrode (PGR/MWCNTPE) and utilized it to detect IP in the aqueous solution. Moreover, IP electro-catalytic oxidation at the PGR/MWCNTPE has been examined by CV, SWV and CA. Values of the catalytic rate constant (k_h=8.42 × 10^3 mol^{-1} L s^{-1}), diffusion coefficient (D=8.73×10^{-5} cm^2/s) and electron transfer coefficient (α=0.49) for IP oxidation have been computed with the use of the voltammetric outputs. Then, a linear calibration curve has been made for IP concentration in ranges between 0.8 and 570 µM with a LOD equal to 0.47 µM IP. Finally, their sensor showed a satisfactory utilization for detecting IP in the medicine and urine specimens [83].

In their study, Ensafi et al. used a ferrocene MWCNTPE to design an electro-chemical technique to detect IP. Therefore, they constructed FCMWCNTPE and demonstrated its electro-catalytic impact for IP electrochemical oxidation. Then, at the optimized conditions of pH=5.0 in CV, IP oxidation happened at a potential around 140 mV less positive than that of the unmodified CPE. Moreover, the kinetics variables like the electron transfer coefficient (α=0.75) as well as catalytic reaction rate constant

(k_h= 1.72×10^2 M^{-1} s^{-1}) have been specified with the use of the electro-chemical methods. Finally, DPV displayed a lower LOD equal to 0.07 μM for IP [84].

Again, Ensafi et al. employed a chemically modified CPE using the N-(3,4-dihydroxyphenethyl)-3,5-dinitrobenzamide (DHPB) and MWCNT as an electro-chemical sensor to detect IP. Then, at the optimized condition, it has been measured with SWV, showing the linear ranges between 0.3 and 125.0 μM of IP and the LOD equal to 0.1 μM. Eventually, RSD for 7 consecutive assays of 1.0 and 20.0 μM IP equaled 1.9 and 2.4% [85].

Another investigation performed by Mazloum Ardakani et al. utilized CV to examine the redox features of a CPE modified by the synthesized oxidized MWCNTs. IP oxidation at the modified electrode happened at a potential around 315 mV less positive than at the unmodified CPE. With regard to DPV, IP oxidation dynamically ranged from 1.0 to 1800.0 μM with the LOD (3σ) of 0.3 μM. Therefore, the electrode has been utilized to detect IP in the synthetic solution and IP injection [86].

Again, Mazloum Ardakani et al. made a CPE modified with 2 - ((7 - (2,5 - dihydro benzylideneamino)heptylimino)methyl) benzene - 1,4 - diol (DHB) and applied CNT for simultaneous detection of IP concentration, folic acid and uric acid in the solution. Thus, at the optimized pH equal to 7.0, IP oxidation happened at a potential around 90 mV less than that of an unmodified CPE. With regard to DPV outputs, IP oxidation dynamically ranged from 10 to 6000 μM and the LOD equaled 1.24 μM [87].

In addition, Beitollahi et al. addressed the synthesis and utilization of 2-Chlorobenzoyl ferrocene (2CBF) for constructing a modified CNTPE. Then, they applied SWV, CA, and CV for studying IP electro-oxidation at the surface of modified electrode. At the optimal condition, SWV peak current of IP showed the linear enhancement with IP concentrations in ranges between 2.5×10^{-7} and 8.0×10^{-5} M so that the LOD equaled 9.0×10^{-8} M for IP. Ultimately, their modified electrode has been utilized to detect IP in the real specimens [88].

In another investigation, Karimi-Maleh et al. utilized 8,9-dihydroxy-7-methyl-12H-benzothiazolo[2,3-b]quinazolin-12-one (DMBQ) modified MWCNTPE to examine electro-oxidation of acetaminophen, tryptophan, IP and their mixture. They showed linear dependence of the peak current on the concentration of IP with the use of SWV in ranges from 0.04 to 400 μM so that the LOD equaled 0.009 μM. Moreover, the modified electrode has been utilized to detect acetaminophen, tryptophan and IP in the drug and biological specimens [89].

Mazloum Ardakani et al. utilized the CPE modified by CNT and benzofuran derivative 1-(4-(1,3-dithiolan-2-yl)-6,7-dihydroxy-2-methyl-6,7-dihydrobenzofuran- 3-yl) ethanone (DDE) in order to electrocatalytically determine IP. Therefore, charge transfer coefficient (α) and constant of the charge transfer rate (k_s) for electron transfer between CPE and benzofuran derivative have been computed to be 0.52 and 1.04 s^{-1}. It has been also found that IP anodic over-potential declined around 256 mV with the use of the above modified electrode. Finally, outputs indicated linear enhancement of DPV peak current of IP followed by their concentration in ranges between 0.05 and 2000.0 μM and thus a LOD of 0.020 μM has been obtained for IP [90].

6. MODIFYING CPE USING NANOCOMPOSITES AND NPs

It is widely accepted that the achievement of nanotechnology has opened new windows for designing and developing the electronic equipment such as the field-effect transistors, light-emitting diodes, detectors, catalyst supports, sensors, lithium ion batteries, solar cells, environmental monitoring, etc. [91]. In addition, experts in the field largely investigated the nanomaterials as a result of their specific structure-dependent features as well as potent utilizations in the multiple applied and basic areas [92-97]. Moreover, as nanomaterials enjoy specific physiochemical features like small dimensions, reasonable stability, bio-compatibility, acceptable conductivity and very good catalytic activities, they are potentially applied for constructing the electrochemical sensors and bio-sensors [98-106].

In this regard, Mazloum-Ardakani utilized a nanostructure electrochemical sensor with a CPE for studying IP electro-catalytic oxidation in the presence of uric acid, tryptophan and folic acid. Therefore, the researchers applied 7-(3,4-dihydroxy-phenyl)-10,10-dimethyl-9,10,11,12-tetra-hydrobenzo[c]acridin-9 (7H)-one (DDTA) and CNPs to examine IP electro-chemical behavior. Then, they computed the obvious charge transfer rate constant (k_s = 1.99 s^{-1}) and transfer coefficient (α= 0.51) for the electron transfer between CPE and modifier. It has been found that at the optimized pH of 9.0, IP oxidation at the modified electrode happened at a potential around 298 mV less positive than the un-modified CPE. Moreover, catalytic rate constant (k=134.28 M^{-1} s^{-1}) as well as diffusion coefficient (D=3.7×10^{-5} cm^2 s^{-1}) have been computed for IP using the CHA technique. In addition, DPV showed 2 linear dynamic ranges of 0.25 to 20.0 µM and 20.0 to 2000.0 µM for IP. Hence, their sensor has been utilized to detect IP from the serum and ampoule specimens. Finally, IP LOD equaled 0.075 µM [107].

In another research, Fouladgar utilized a synthesized IL (1-Methyl-3-butylimidazolium bromide) and ZnO NPs to modify CPE. They employed the modified electrode for IP detection. At the optimized pH equal to 7.0, IP oxidation in the presence of ZnO NPs and IL took place at a potential around 520 mV and oxidation current has been shown to be above the unmodified electrode. In addition, SWV has been utilized to detect the method linear dynamic range. Moreover, analyses showed linearity of the oxidation current plot versus the concentration in ranges between 0.08 and 800.0 µM IP and LOD equaled 0.04 µM IP. Researchers specified diffusion coefficient (D=2.9×10^{-6} cm^2 s^{-1}) and electron transfer coefficient (α 0.78) for IP with the use of the electro-chemical strategies. It is notable that their method has been explored to detect IP in the biological and drug specimens [108].

The study performed by Mazloum Ardakani et al. exploited a CPE modified with (E)-2-((2-chloro-phenylimino) methyl) benzene-1,4-diol (CD) and TiO_2 NPs for preparing an electro-chemical sensor. Outputs indicated efficacious catalytic activities of the electrode for IP electrooxidation that declined its over-potential by above 235 mV. Then, researchers computed values of the catalytic rate constant (k_h=(1.1±0.05)×10^3 M^{-1} s^{-1}), diffusion coefficient (D=(3.4±0.14)×10^{-5} cm^2s^{-1}) and electron transfer coefficient (α = 0.35) for IP with the use of electro-chemical strategies. Considering DPV, IP oxidation dynamically ranged from 0.5 to 1000 µM and LOD (3σ) equaled 0.47 µM. Moreover, DPV has been utilized to simultaneously determining IP, folic acid and acetaminophen at the modified electrode. Notably, the above technique has been employed to detect IP in the real specimen with standard addition procedure [109].

Mohammadi et al. utilized a CPE modified with IL (n-hexyl-3-methyl-imidazolium hexa-fluoro phosphate) and magnetic core-shell NPs (MCSILCPE) to make IP electro-chemical nanosensor. Then, DPV showed a linear dynamic range between 1.0×10^{-6} and 7.0×10^{-4} M IP. LOD equaled 6.3×10^{-7} M and electrode has been exploited for determining IP in the real specimens [110].

In their study, Karimi-Maleh et al. devised a sensor on the basis of ZnO NPs/IL composite for the voltammetric sensing of IP in the real specimens. In addition, the modified CPE (ZnO NPs/IL/CPE) has been utilized as one of the electro-chemical sensors to determine the trace amounts of IP. Moreover, complete separation of IP anodic peaks and aspirin has been observed in their mixture. Furthermore, at pH of 5.0, 2 peaks have been separated ca. 0.56 and 0.98 V; thus, IP may be detected in the presence of aspirin and above 2.6 times of the current surplus of IP. Consequently, SWV peak current of IP showed a linear elevation with their concentration in ranges between 0.3 and 320 µM IP. As a result, LOD for Ip equaled 0.09 µM. Their sensor showed a successful utilized to assay IP in the real specimens like urine and medicine [111].

The study conducted by Pourtaheri et al. co-detected IP as well as paracetamol in the aqueous solution via devising and synthesizing a new sensor on the basis of *N*-(ferro-cenylmethylidene)fluoren-2-amine-modified CPE (La^{3+}/ZnONFMF2ACPE) and the feather-like La^{3+}/ZnO nanoflower (NFs). Therefore, the plot of a linear calibration curve has been drawn for distinct concentrations of IP (0.1 to 400.0 µM) with 0.05 µM LOD. At the end, reasonable outputs have been attained following IP and paracetamol detection in the humans' urine, serum, and medicine real specimens with the use of the newly developed sensor [112]. The comparison of several parameters of IP for the all above mentioned CPEs is summarized in Table 1.

Table 1. Analytical functions observed by the IP electro-chemical detection via the various modified CPE.

Electrochemical method	Modifier	Linear range	Detection limit	Ref.
SWV	BBFT/Gr	6.0×10^{-8}-7.0×10^{-4} M	12.0 nM	[62]
SWV	EFTA/Gr	0.1-600.0 µM	0.034 µM	[63]
DPV	CNPs/ RGO/NYB	0.5-1000.0 µM	0.065 µM	[64]
SWV	3,4'-AA/GO	2.5×10^{-8} - 2.0×10^{-5} M	12 nM	[65]
SWV	RGO/CNT/CBE	0.125-300.0 µM	50.0 nM	[66]
DPV	2,7-BF/CNT	0.08-700.0 µM	26.0±2 nM	[76]
SWV	5ADMB/CNT	0.09-400.0 µM	39.0 nM	[77]
DPV	molybdenum (VI) complex-CNT	0.7-600.0 µM	35.0 nM	[78]
DPV	CNT/5ABD	4.0×10^{-7} - 9.0×10^{-4}M	2.0×10^{-7} M	[79]
DPV	MWCNT/IL	1.0- 520 µM	0.85 µM	[80]
DPV	FMA-CNT	0.5- 50.0 µM	0.2 µM	[81]
DPV	p-chloranil/CNT	0.015–100 µM	0.009 µM	[82]
SWV	PGR/MMWCNT	0.8-570 µM	0.47 µM	[83]
DPV	ferrocene /MWCNT	0.1-0.6 µM	0.07 µM	[84]

DPV	DHPB/MWCNT	0.3-125.0 µM	0.1 µM	[85]
DPV	OMWCNTs	1.0-1800.0 µM	0.3 µM	[86]
DPV	DHB/CNT	10-6000 µM	1.24 µM	[87]
SWV	2CBF/CNT	2.5×10^{-7} - 8.0×10^{-5} M	9.0×10^{-8} M	[88]
SWV	DMBQ/MWCNT	0.04-400.0 µM	0.009 µM	[89]
DPV	DDB/MWCNT	0.05-2000.0 µM	0.020 µM	[90]
DPV	CNPs/DDTA	0.25-2000.0 µM	0.075 µM	[107]
SWV	ZnO NPs/IL	0.08- 800.0 µM	0.04 µM	[108]
DPV	TiO_2 NPs/CD	0.5 - 1000 µM	0.47 µM	[109]
DPV	MCS NP /IL	1.0×10^{-6} -7.0×10^{-4} M	6.3×10^{-7} M	[110]
SWV	ZnO NP/IL	0.3-320 µM	0.09 µM	[111]
DPV	La^{3+}/ZnO NFs/ NFMF2A	0.1–400.0 µM	0.05 µM	[112]

7. SURFACE MODIFICATION OF GLASSY CARBON ELECTRODE (GCE)

GCE is the commonest electrode utilized for electro-chemical sensing of IP as a result of the respective great electrical conductivity, higher chemical resistance, very good mechanical stability, impermeability to the gas, and most importantly the broadest potential ranges of each carbon electrode or larger electro-chemical windows [113-118]. It has been found that GCE has a rapid electro-kinetics as a result of their higher electron transfer rate on the surface of electrode and the response is more rapid in comparison with the thin-film metal electrodes that may have a relationship to larger diameter of the working area. According to its adjustable surfaces, GCE may be readily modified via electro-polymerizing the inert organic monomers [119] or coating the protecting modifiers or polymers on the top of electrode with Nafion [120]. However, the key benefit of GCE is possible re-utilization via polishing surfaces. Because of the respective physico-chemical features, GCE has become one of the encouraging commonly utilized electrodes that has a rather high chemical inertness.

In their study, Beitollahi et al. built a GCE modified with Gr and hematoxylin. Moreover, electro-chemical examination of the modified electrode and its effectiveness for electrocatalytically oxidizing IP has been explained. Based on the findings, IP oxidation at the surface of modified electrode happened at a potential of nearly 345 mV less positive than that of the un-modified GCE. Additionally, LOD of 5.0×10^{-7} M for IP has been attained with the SWV. Ultimately, modified electrode has been utilized to simultaneously determine acetaminophen, tyrosine and IP in the biological and drug specimens [121].

Moreover, Wong et al. examined using the GO, carbon black (CB), poly3,4-ethylene-dioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS) and Cu NPs as the electrode substances to simultaneously detect acetaminophen, IP, propranolol, caffeineas and folic acid. In addition, with the use of the SWV, organized as well as resolved anodic peaks have been determined for acetaminophen, IP, propranolol, caffeine and folic acid with the peak to peak potential separation at least of 170 mV. In the next step, SWV has been examined to simultaneously determine the quinary mixes of the analytes, which led to the analytical curves with a linear range between 8.0 and 50 µM and LOD equal to 1.9 µM

for IP. Consequently, functional viability of their voltammetric sensor has been demonstrated for analyzing the humans' body fluid specimens. Finally, their sensor exhibited acceptable iterability and a substantial utilization with serum and urine matrices with recovery approximated to 100% [122].

In another investigation, Chen et al. examined IP electro-chemical detection with the use of a Gr modified GCE. According to the outputs, GCE had very good electro-chemical activities toward IP at pH of 4.0 PBS. IP reduction peak current (i_{pc}) has been linearly proportionate with its concentration in a range between 2.1×10^{-7} and 1.0×10^{-5} M and 1.0×10^{-5} and 1.0×10^{-4} M and LOD equal to 6.4×10^{-8} M. It is notable that their technique showed a successful application for analyzing the IP samples [123].

Moreover, Palakollu et al. concentrated on the fabrication of an electro-chemical sensor for IP, which has been consisted of β-Cyclodextrin (β-CD) functionalized GO and an electro-chemically produced acid yellow 9 polymer as a composite substance modified GCE (β-CD-GO/PAY/GCE). Figure 2 depicts the detailed preparation process of β-CD-GO/PAY/GCE. LOD at β-CD-GO/PAY/GCE equaled 3.3×10^{-8} M for IP [124].

In addition, Mazloum-Ardakani and Khoshroo synthesized and applied the functionalized MWCNTs with TiO_2 NPs, 9-(1,3-dithiolan-2-yl)-6,7-dihydroxy-3,3-dimethyl-3,4-di-hydrodibenzo[b,d]furan-1(2H)-one (benzofuran derivative (DDF)) and 1-butyl-3-methyl-imidazolium tetra-fluoroborate (IL) as the sensitive sensor for simultaneously determining IP and serotonin with the use of GCE. According to the DPV data, anodic peak currents had a linear dependence on IP concentration in the range between 0.1 and 1300.0 μM and utility of the modified electrode has been verified via simultaneously determining serotonin and IP in the human serum [125]. In this study, Mazloum Ardakani et al. proposed GCE chemically modified with MWCNT (z)-1-(3,4-dihydroxy-benzylidene)-2-methyl-thiosemicarbazide (DBT-MWCNT/GCE). Therefore, they specified the kinetic variables like anodic transfer coefficient (α=0.47) and constant of the electron transfer rate between nanocomposite and GCE (ks/s=0.51). Outputs indicated a linear correlation versus the concentration of IP in the broad ranges between 0.5 and 1500.0 μM and a LOD equal to 0.35 μM. Consequently, researchers employed DPV to simultaneously determine piroxicam and IP [126].

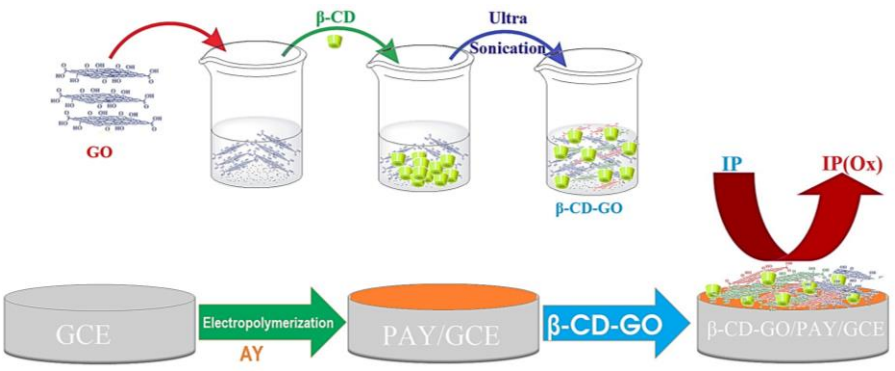

Figure 2. Step-wise procurement of β-CD-GO/PAY/GCE. Reused with permission from Ref. [124] Copyright 2017 Elsevier.

Mazloum Ardakani et al. substantially employed a new layer-by-layer assembly of the Au NPs and 2-(2,3-dihydroxy phenyl) benzo-thiazole (DPB) at a GCE (GCE/AuNPs/DPB). They utilized GCE/AuNPs/DPB for simultaneously determining uric acid and IP and DPV demonstrated a linear dynamic range in a concentration range between 0.1 and 900.0 μM and the LOD (3σ) equal to 82 nM for IP under the optimized condition. Finally, DPV has been applied to detect IP in the real specimens [127].

Another investigation by Mazloum Ardakani et al. utilized molecular self-assembled mono-layers of 5-(1,3-dithiolan-2-eyl)-3-methyl banzen-1,2-diol (DMD) on the Au NPs (DMD-Au NPs). In addition, CV has been employed for examining redox features of the modified electrode at diverse scan rates. Then, a pair of the organized quasi-reversible redox peaks of DMD have been observed at the modified electrode and thus a remarkably augmented electro-catalytic activity has been observed at the DMD-Au NPs as one of the electro-chemical sensors for investigating IP electro-oxidation. Using their modified electrode, IP oxidation potential shifted nearly 235 mV towards a less positive potential value in comparison with the unmodified electrode. Researchers also computed value of electron transfer coefficient (α=0.5), diffusion coefficient ($D=8.9\times10^{-5}$ cm^2 s^{-1}) and catalytic rate constant ($k_s=9.2$ s^{-1}) for IP. Moreover, responses of the catalytic current with IP concentration implied the linear correlation in a range between 0.5 and 800 μM with the LOD of 0.21 μM. Finally, the new modified electrode has been utilized to detect IP in IP injection [128].

A nanocomposite (GCE/AuNP-DAT) has been built by Mazloum Ardakani et al. using the self-assembly of a thiophenol derivative (3,4-dihydroxyphenyl-azo-2-thiophenol, DAT) on a Au NP-modified GCE. The electrode was utilized as a sensor and DPV data achieved with their sensor showed a linear dynamic range from 1 to 1500 μM and a LOD equal to 0.46 μM for IP [129].

In another study, Shahrokhian et al. addressed the synthesis of the hollow carbon spheres (HCS) as well as hollow nitrogen-doped carbon spheres (HNCS) via 2 distinct techniques. Then, electro-chemical behaviour of IP has been analyzed on the GCE surface modified with HNCS and HCS. Moreover, modifying GCE with the HNCS considerably elevated in the oxidation peak current of IP as a result of the higher electro-chemical conductivity as well as larger active surface areas. Based on the optimized experimental condition, LSV has been utilized to detect distinct concentrations of IP with the use of HNCS/GCE. In addition, 2 dynamic linear ranges of 0.2-2.0 and 2.0-30 μM with the LOD equal to 60 nM has been achieved with the modified electrode for IP voltammetric detection. Furthermore, outputs of examination indicated successful utilization of this technique for accurately determine the trace amounts of IP in the clinical and drug preparation [130].

Moreover, Dhanalakshmi et al. devised an electro-chemical sensor with 3% lanthanum doped zinc oxide with RGO (3% LZO/RGO) nano-hybrid for sensitive and selective detection of IP. In addition, 3% LZO/RGO nano-hybrid had the greatest electro-catalytic activities toward IP determination. Their sensor exhibited a broad linear range (0.01 to 700 μM) with LOD equal to 7.23 nM (at S/N=3). Then, sensitivity has been computed to be 0.49 μA μM^{-1} cm^{-2} [131]. The comparison of several parameters of IP for the all above mentioned GCEs is summarized in Table 2.

Table 2. A number of analytical functions observed by the IP electro-chemical detection via the GCE modified with different modifiers.

Electrochemical method	Modifier	Linear range	Detection limit	Ref.
SWV	Hematoxylin/Gr	1.0×10^{-6} - 8.0×10^{-4}	5.0×10^{-7} M	[121]
SWV	CB/GO/ CuNPs PEDOT:PSS	8.0-50.0 μM	1.9 μM	[122]
DPV	Gr	2.1×10^{-7} -1.0×10^{-4} M	6.4×10^{-8} M	[123]
DPV	β-CD-GO/PAY/GCE	1.0-52.0 μM	3.3×10^{-8} M	[124]
DPV	MWCNT/DDF/TiO_2 NP/IL	0.1-1300 μM	28 ± 2 nM	[125]
DPV	DBT-MWCNT	0.5-1500.0 μM	0.35 μM	[126]
DPV	AuNPs/DPB	0.1-900.0 μM	82 nM	[127]
DPV	DMD-AuNPs	0.5-800 μM	0.21 μM.	[128]
DPV	AuNP-DAT	1-1500 μM	0.46 μM	[129]
LSV	HNCS	0.2-30 μM	60 nM	[130]
DPV	3% LZO/RGO	0.01−700 μM	7.23 nM	[131]

8. SURFACE MODIFICATION OF SCREEN-PRINTED ELECTRODE (SPE)

According to the previous studies, utilization of the SPEs rather than traditional electrodes like GCEs or CPE involves in showing a number of procedures in the analytical chemistry like miniaturization [132-135]. Electro-chemical sensors on the basis of SPEs match the needs of in-situ screening tools in each portable device for electro-chemical analysis. In fact, SPEs possess all key function features of the sensors, their sample is minimally prepared, they are fast, inexpensive, and can be easily utilized. Moreover, they are small, which may be miniaturized with the novel technology [136-139].

We procured graphene quantum dots (GQDs) through adjusting carbonization degree of citric acid. Moreover, Dourandish and Beitollahi fabricated the graphite SPE modified with GQDs (GQDs/SPE) for sensitive voltammetric detection of IP. As compared to the un-modified electrode, presence of the GQD/SPE remarkably enhanced in the peak currents. Therefore, the modified electrode exhibited acceptable electrical conductivity with reasonable electro-chemical responses to IP. In addition, GQDs/SPE displayed linear ranges between 1.0 and 900.0 μM and a LOD equal to 0.6 μM (S/N=3) to IP [140]. Table 3 briefly present IP variables for this SPE.

Table 3. The IP variable of SPE.

Electrochemical method	Modifier	Linear range	Detection limit	Ref.
DPV	GQDs	1.0 to 900.0 μM	0.6 μM	[140]

9. CONCLUSIONS

Continual developments of the novel substances have a significant role in advancement of the IP detection procedures. Recently, researchers performed a lot of investigations on the developed substances. Several devices are provided for electrochemically analyzing IP that include the bare electrodes of diverse substances to the electrodes modified with compounds, which may considerably ameliorate sensitivity. Therefore, this review addressed benefits of the electro-chemical procedures to analyze IP with the use of different kinds of electrode substances. In fact, electro-chemical techniques with various kinds of electrode substances have manifested as one of the encouraging fields. However, each approach has its own benefit and restriction. Hence, we reviewed promotion of the determination sensitivity with regard to modifying diverse kinds of electrodes with the use of graphene, graphene oxide, carbon nanotubes, nanocomposites as well as NPs substances. Hence, there will be several areas that should be additionally explored.

CONFLICTS OF INTERESTS
The authors declare that they have no competing interests.

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