

Anion-Doped Overoxidized Polypyrrole/Multiwalled Carbon Nanotubes Modified Glassy Carbon Electrode as a New Electrochemical Sensing Platform For Buprenorphine Opioid Drug

Abdolhamid Hatefi-Mehrjardi^{*1}, Soghra Rafiei Boldaji^{1,2}, Mohammad Reza Yaftian², Hassan Shayani-Jam²

1. Department of Chemistry, Payame Noor University (PNU), P.O. Box 19395-4697, Tehran, Iran

2. Department of Chemistry, Faculty of Science, University of Zanjan, P.O. Box 45371-38791, Zanjan, Iran

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Abstract

A novel Buprenorphine (BPR) sensor is fabricated based on nanocomposite film of benzene-1,3-disulfonate anion doped overoxidized polypyrrole/multiwalled carbon modified glassy carbon electrode. The carbon nanotubes were drop-casted on bare electrode, and then thin layer of benzene-1,3-disulfonate-doped overoxidized polypyrrole formed electrochemically on it. Effect of experimental conditions involving supporting electrolyte pH, carbon nanotubes suspension drop size, and the number of potential cycles in overoxidized polymerization were optimized by monitoring the voltammetry responses of the modified electrode. Then the optimized modified electrode was used for electrochemical sensing of BPR by differential pulse voltammetry, which exhibited a linear growth with high sensitivity in anodic peak currents at the BPR concentration range of 0.06-40 μ M, and a detection limit of 28 nM. Finally, the determination of BPR in urine real samples was performed by the new sensor and satisfactory results obtained.

Keywords: Buprenorphine; Multiwalled Carbon Nanotubes; Overoxidized Polypyrrole; Nanocomposite; Electrochemical Sensor; Differential Pulse Voltammetry.

1. INTRODUCTION

Drug abuse is an earnest health problem in our society and is currently one of the most significant concerns of governments [1]. Opioids are a group of drugs that stimulate the brain to increase pleasant feelings. Medication with some opioids, namely narcotics, is given to treat pain and the other health difficulties. Dependency is the main side effects of opioid medication misuse, which sometimes results in addiction. Buprenorphine (BPR) a derivative of the opioid alkaloid thebaine identified as a potentially valuable drug for the efficient and safe treatment of opioid addiction, from nearly five decades ago [2]. Commonly, it used at higher doses for opioid addiction treatment and at lower doses for reducing both moderate chronic pains and moderate to acute pains in nonopioid-tolerant individuals [3]. The extensive use of BPR in medicine had been resulted in developing various methods for its determination in biological specimens. Analytical techniques currently reported for determination of BPR include electropray mass spectrometry [4,5], gas chromatography [6-7][8]9], liquid chromatography [10,11], and high-performance liquid chromatography [12,13]. Although these techniques are suitable and sensitive enough for

BPR determination but have several disadvantages, such as expensive, time-consuming, need sample pretreatment steps and produce a great amount of liquid waste [14]. Electrochemical methods because of some advantages such as rapidity, high sensitivity, good selectivity, and easy preparation have increasing attention for routine analysis [15]. A few researchers were used voltammetry techniques in the determination of BPR on carbon paste electrodes [16]. Fakhari et al. reported the determination of BPR with a screen-printed carbon electrode [17]. Behpour et al. applied a carbon paste electrode and SDS as an enhancement factor for the determination of BPR [18]. Carbon nanotubes with one-dimensional cylindrical nanostructure have high electrical conductivity, large surface area, mechanical and thermal stability, and other unique properties [19,20]. Conducting polymers are poly-conjugated organic polymers that have physical and chemical structures of conventional organic polymers along with metals electronic properties. In the last two decades, conducting polymers have emerged as favorable electrode material in the fabrication of chemical sensors and biosensors. Polypyrrole (PPY) is the most prominent conducting polymers that has received

*Corresponding Author: hhatefy@pnu.ac.ir; hhatefy@yahoo.com

significant attention as an electrode modifier because of excellent conductivity, the aqueous solubility of the monomer, low cost, highly stable, easy synthesis from aqueous solutions, effective polymerization, and thin layer with controllable thickness [21-22][23][24][25]. Over-oxidation of PPY film at higher potentials leads to the formation of porous structure and large surface area. Furthermore, in the over-oxidation process, some carbonyl and carboxyl groups introduce in pyrrole rings of the PPY film, resulting in improvement of the permselective and antifouling properties of the sensor [26]. Electropolymerization of PPY on carbon nanotubes results in new nanocomposite, which has complementary and distinct properties of each component along with a synergistic effect. The application of such new nanocomposites with improvement in mechanical and electrochemical properties leads to higher performance of the resultant sensing devices.

The present work develops a simple and versatile in situ approach for the fabrication of a nanostructured thin film composite (as a modifier) on the surface of a glassy carbon electrode by overoxidized electropolymerized pyrrole doped with benzene-1,3-disulfonate anion at the surface of a precast MWCNTs film. Characterization of the modified electrode was performed by scanning electron microscopy (SEM), and the experimental parameters optimized for sensitive voltammetry determination of BPR.

2. EXPERIMENTAL

2.1. Materials

Buprenorphine hydrochloride was prepared from TEMAD[®] Pharmaceutical Company (Tehran, Iran) and used without further purification. Pyrrole, sodium benzene-1,3-disulfonate (SBDS), dimethylformamide (DMF), and all of the other reagents were of the analytical grade that prepared from Merck (Darmstadt, Germany). MWCNTs with high purity were prepared from the Research Institute of Petroleum Industry (RIPI, Iran). Preparation of phosphate buffer saline (PBS) solutions was carried out by mixing the NaClO₄ (0.1 M) and H₃PO₄ (0.01 M) solutions, followed by the pH adjustment with NaOH (0.11 M). A freshly calibrated pH/Ion meter (Metrohm) was survived for pH adjustments. All of the experiments were carried out at room temperature. All of the solutions were prepared with deionized water.

2.2. Apparatus

A Potentiostat/Galvanostat Autolab 12 that controlled with GPES 4.9 software (Eco Chemie B.V., The Netherlands) on a 32-bit personal

computer platform was survived for electrochemical experiments. A set of the electrochemical cell includes 100 ml standard glass cell containing a glassy carbon (GCE, 2-mm diameter, Azar) as working electrode, Ag/AgCl (Sat'd KCl, Metrohm) as reference electrode and platinum bar (Metrohm) as the auxiliary electrode was used in all electrochemical experiments. Field-emission scanning electron microscopy (FESEM-TESCAN MIRA3) was used for morphological investigation.

2.2. Electrode modification

The bare GCE with a clean and smooth surface was obtained by several times polishing on special polishing cloth, including aqueous slurries of alumina (0.05 mm) and then thoroughly rinsed with double distilled water. The cleaned GCE was dried at room temperature and used immediately for modification. Functionalization and purification of MWCNTs were performed by dispersion in the mixture of 1:3 nitric acid:sulfuric acid solution for 24 h. After filtration and rinsing with double distilled water, it was oven-dried entirely, and then 5 mg of it was dispersed in DMF solvent (5 mL) by ultrasonication in an ultrasonic bath for 30 min. Different dropping volumes of MWCNTs suspension were dropped on the GCE surface and then placed in oven 50°C for 40 min to remove DMF. The modified electrode is shown as MWCNTs/GCE. The polypyrrole (PPY) film on MWCNTs/GCE was made by cyclic voltammetry in the potential range of 0 - 0.8 V with the sweep rate of 0.05 V/s for 15 repetitive cycles in an aqueous pyrrole (5 mM) solution containing SBDS (3 mM) as dopant anion. Then, the modified electrode was washed with double distilled water, and overoxidation of the PPY film was performed by ten repetitive potential cycling between -0.20 and +1.30 V (scan rate 0.10 Vs⁻¹) in PBS (0.11 M, pH 7.0) and a reproducible background current was obtained.

3. RESULT AND DISCUSSION

3.1. Morphological and voltammetry characterization

The FESEM images were used to investigate the morphological characteristics of MWCNTs film, and OPPY nanocomposite film coated glassy carbon electrodes. Fig. 1 (a) and (b) show that the electrode surface entirely covered by homogenous film. Nanosized structure and large surface area of pristine MWCNTs make it a suitable substrate for the electropolymerized PPY. The highly uniform nanoporous OPPY/MWCNTs film that formed via layer-by-layer deposition leads to enhancement of the microscopic area of the electrode and higher sensitivities in the

electrochemical measurements. As cyclic voltammograms showing in Fig. 2, anodic oxidation currents grow during the electropolymerization of doped PPY film that indicates the formation of consecutive and controllable conductive film at the surface of MWCNTs/GC electrode.

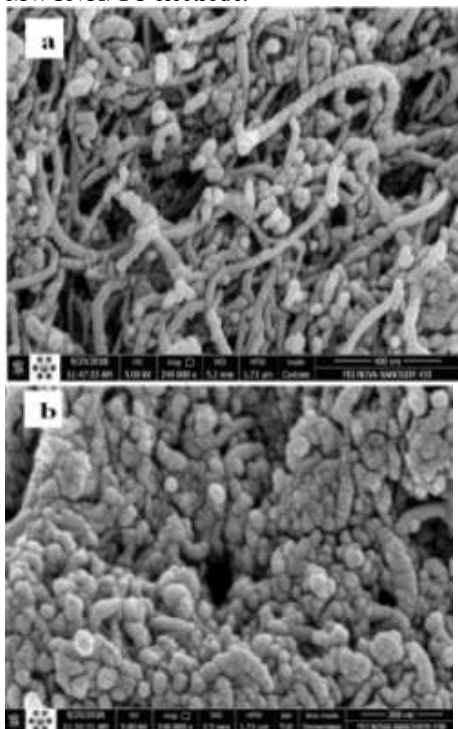


Fig. 1. FESEM images of (a) MWCNTs and (b) OPPY/MWCNTs modified GCE.

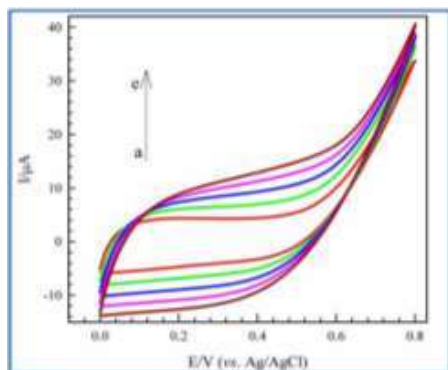


Fig. 2. Successive cyclic voltammograms obtained during the electropolymerization of 5 mM pyrrole, in the presence of 3 mM SBDS as dopant agent on the surface of MWCNTs/GCE. The a-e correspond to 3rd, 6th, 9th, 12th, and 15th scans. The sweep rate is 0.05 V s⁻¹.

3.2. Electrochemical behavior of BPR

The cyclic voltammograms of bare and modified GCE was obtained in PBS (0.11 M, pH 3.0) containing 10.0 μM BPR (Fig. 3). As can be seen,

BPR has a well-defined oxidation peak on bare and the two modified GCE.

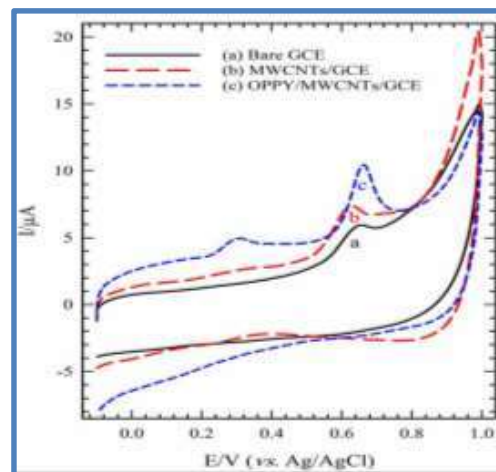


Fig. 3. Cyclic voltammograms of (a) bare GCE, and modified GCE with (b) MWCNTs and (c) OPPY/MWCNTs in PBS solution (0.11 M, pH 3.0) containing 10 μM of BPR with accumulation time 120 s and potential sweep rate of 100 mV s⁻¹.

The enhancement in the background currents of MWCNTs/GCE and OPPY/MWCNTs/GCE (Fig. 3 b, and c) relative to bare GCE (a) indicated larger active surface areas of MWCNTs. Also, the BPR anodic peak current is improved at the OPPY/MWCNTs/GCE surface that showed higher conductivity and facilities in electron transfer related to the OPPY layer at the MWCNTs modified electrode surface.

Table 1. Peak's characteristics of the three cyclic voltammograms in Fig. 3.

Electrode	E_p/V	$I_p/\mu A$
Bare GCE	0.656	1.23
MWCNTs/GCE	0.630	2.75
OPPY/MWCNTs/GCE	0.309, 0.662	1.012, 4.487

MWCNTs layer act as a proper nanosized substrate for electropolymerization of pyrrole, and the whole MWCNTs surface on the electrode was covered by homogenous polymeric film, which improves adsorption of BPR on the electrode surface. Furthermore, an additional oxidation peak can be detected at 0.309 V on the OPPY/MWCNTs/GCE (Fig. 3, curve c). It should be noted that adsorption of electro-oxidized BPR on the surface of polymeric film followed by consecutive electro-oxidation reaction results in the second peak at the OPPY/MWCNTs/GCE [27].

3.3. Influence of pH

Electrochemical oxidation of BPR strongly depends on the pH of solution due to the

existence of two electroactive groups (phenolic and N) in the structure. The pH of PBS (0.11 M) containing 10 μM BPR was changed in the range of 3 to 10, and then the cyclic voltammograms of the OPPY/MWCNTs/GCE were recorded (Fig. 4A). Maximum anodic peak current was obtained in solution of PBS (0.11 M) at pH=3.0 (Fig. 4B). As can be seen in Fig. 4C, with an increase in pH, the anodic peak potential of BPR shifts to the less anodic potentials. Additionally, the slope 0.0558 V/pH is obtained from the linear plot of E_p vs. pH. The closeness of this slope to the theoretical (59 mV/pH) value at 25°C indicated the number of electrons is the same as protons numbers involved in the oxidation process of BPR [18].

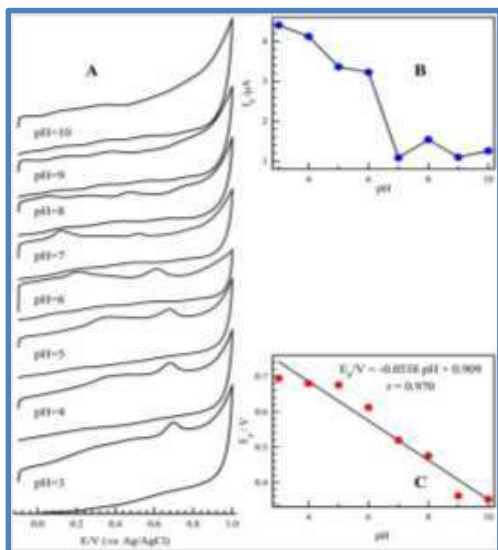


Fig. 4. Cyclic voltammograms of OPPY/MWCNTs/GCE in PBS (0.11 M) solutions containing 10 μM BPR with pH range 3.0 - 10.0 (A). The extracted peak currents (B) and peak potentials (C) vs. pH. The sweep rate is 100 mVs^{-1} , and the accumulation time is 120 s.

3.4. Influence of the amounts of MWCNTs and OPPY

The sensitivity of OPPY/MWCNTs/GCE is strictly depends on the amounts of MWCNTs and OPPY modifiers (Fig. 5). Therefore, in order to the optimization of MWCNTs quantity, different volumes (1 – 5 μL) of the suspension of MWCNTs (1 mgmL^{-1}) were cast on the surface of GCE and then the electropolymerization was performed by 15 sweeps in pyrrole solution. The variation of anodic peak current with the volume of MWCNTs suspension is shown in Fig. 5A. At a very low amount of MWCNTs (a skinny film), the BPR peak current is in minimum amount. By increasing the amount of MWCNTs suspension

up to 3 μL , the BPR oxidation peak current is growth. Its higher amounts cause to increasing in background currents and decreasing BPR anodic peak current. Therefore, 3 μL of MWCNTs suspension (1 mgmL^{-1}) was selected as the optimum amount. Furthermore, in order to the optimization of OPPY amount, different numbers of the potential sweeps were applied to the electropolymerization of pyrrole on the optimized MWCNTs modified GCE. The variation of anodic peak currents with the number of potential sweeps is shown in Fig. 5B. By increasing the number of potential cycles up to 15 cycles, the BPR anodic peak current reaches to its maximum value, and more electropolymerization, results in passivation of the electrode surface and weaken the voltammetry responses.

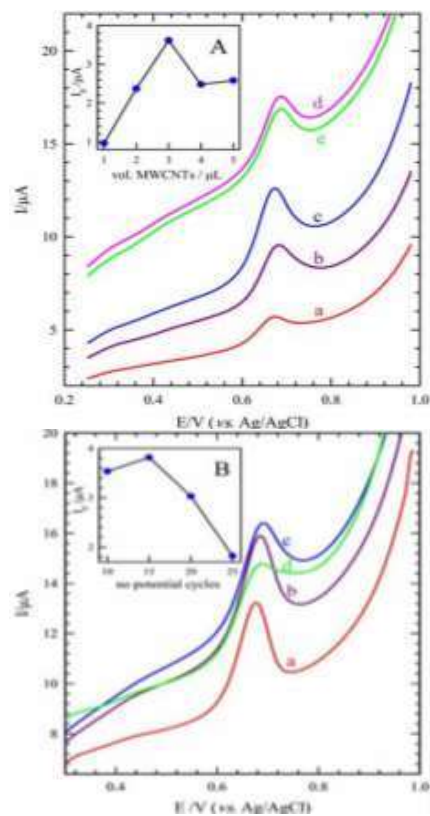


Fig. 5. LSVs of 10.0 μM BPR in PBS (0.11 M, pH 3.0) related to the OPPY/MWCNTs/GCE with (A) several amounts (1,2,3,4 and 5 μL , 1 mgmL^{-1}) of MWCNTs suspension, and (B) several number of the potential sweeps (10, 15, 20 and 25) for electropolymerization of pyrrole with potential scan rate 100 mVs^{-1} , and accumulation time 120 s.

3.5. Influence of potential sweep rate

The effect of potential sweep rate (v) on the electrooxidation of BPR at the surface of OPPY/MWCNTs modified GCE in the range 20-

200 mVs⁻¹ was studied by LSV (Fig. 6). In order to find the BPR electrooxidation reaction mechanism at the modified electrode surface, the correlation between the potential sweep rate and the peak current was studied.

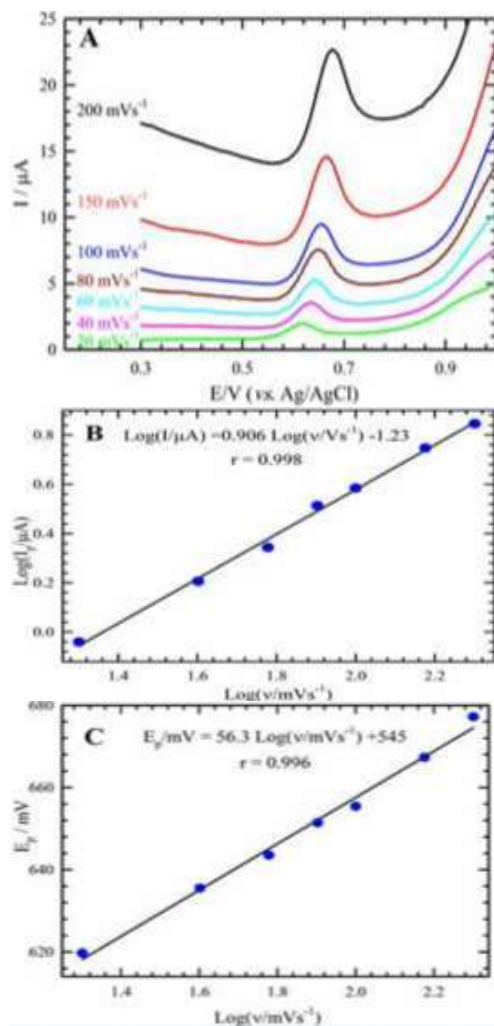


Fig. 6. (A) LSVs of optimized OPPY/MWCNTs/GCE at various sweep rates in PBS solution (0.11 M, pH 3.0) containing 10 μM BPR. Correlations of (B) logarithm of anodic peak currents and (C) anodic peak potentials with logarithm of scan rates. The accumulation time was 120 s.

As can be seen in Fig. 6B, there is a linear relationship between the logarithm of BPR anodic peak current (I_p) and the logarithm of the sweep rate. This behavior represents a mixed diffusion - adsorption controlled process for the electrode reaction [28]. Also, by increasing the scan rates, the peak potentials shift toward more anodic potentials. As is shown in Fig. 6C, there is a linear relationship between the logarithm of potential sweep rate and the BPR anodic peak

potential. This behavior is expected for the irreversible electrochemical reaction [29]:

$$E_{p,a} = (1/2)b \log v + \text{constant} \quad (1)$$

where b is the Tafel slope. From Fig. 6C, the slope is 56.3 mV; therefore, the Tafel slope is 112.6 mV, which is consistent with the transfer of one electron in the rate-determining step.

3.6. Analytical Performance

Differential pulse voltammetry (DPV) technique is applied for BPR sensitive determination by using OPPY/MWCNTs modified GCE. Fig. 7A shows the DPVs related to oxidation of various BPR concentrations at the optimum experimental conditions. The BPR calibration curve consists of oxidation peak currents related to various BPR concentrations was recorded (Fig. 7). The BPR oxidation peak currents are changed linearly with the variation of BPR concentration in the range of 0.06 – 40.0 μM according to the following equation:

$$I_{p,a}/\mu\text{A} = 0.439C_{\text{BPR}}/\mu\text{M} + 1.16; r = 0.997 \quad (2)$$

The detection limit (DL) based on the signal-to-noise ratio of 3 was calculated 28 nM. The relative standard deviation (RSD) results for the repeatability of BPR sensing with OPPY/MWCNTs/GCE, was calculated for the peak currents of five repetitive DPVs in the PBS (0.11 M, pH=3.0) solution containing 8.0 μM BPR. It was 2.2% showing good repeatability and precision.

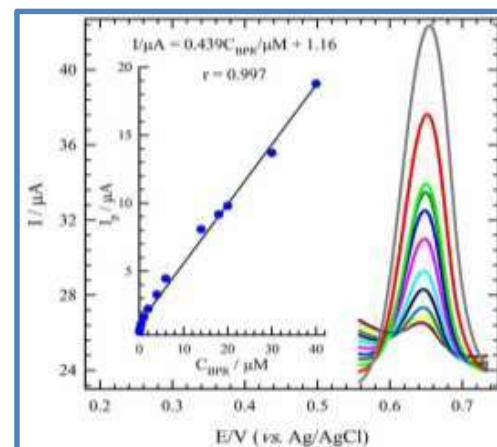


Fig. 7. Differential pulse voltammograms of OPPY/MWCNTs/GCE in PBS (0.11 M, pH=3.0) solution containing various concentrations of BPR. The inset shows the related calibration line at the concentration ranges of 0.06-40 μM. The accumulation time was 120 s.

3.7. Real Sample Analysis

The reliability of the proposed modified electrode was tested in human urine real samples. Each urine sample diluted 50 times

with PBS (0.11 M, pH=3.0) solution. The recovery was evaluated by employing the standard addition method. The recovery of the spiked samples was obtained in the range of 97.88 - 103.49, which confirmed the applicability of the OPPY/MWCNTs modified GCE for BPR determination in urine matrixes (Table 2).

Table 2. The recovery test results of BPR determination in urine real samples.

No. sample	Added (μM)	Found (μM)	Recovery (%)
1	2	1.98	97.8
2	4	4.13	103.2
3	10	10.50	105

In Table 3, performance of the fabricated BPR sensor in this work is compared with the reported values from the other modified electrodes. As can be seen, the OPPY/MWCNTs/GCE has an acceptable detection limit and a wide linear range in comparison to some of the previously reported sensors.

Table 3. Comparison of the figures of merits related to different modified electrodes for BPR detection by DPV method. r-GO/SPCE: reduced-graphene oxide/screen-printed carbon electrode; SDS/CPE: sodium dodecyl sulfate/carbon paste electrode; CS/MNCs: citrate stabilized/magnetic nanocrystal.

Modified electrode	Linear range (μM)	LOD (nM)	Reference
r-GO-SPCE	0.5-100	160	[17]
SDS/CPE	0.004-0.126, 0.126-0.317	1.3	[18]
CS-MNCs/CPE	0.02-68.0	4.3	[30]
OPPY/MWCNTs/GCE	0.06-40.0	28	This work

4. CONCLUSION

This work reports an efficient and low-cost method for preparation of anion-doped OPPY/MWCNTs nanocomposite modified GCE that applied for BPR detection. The proposed sensor exhibited some advantages such as wide linear range, low detection limit, good sensitivity and selectivity, low cost, and easy preparation of the modified electrode.

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عبدالحمید هاتقی مهرجردی^۱، صغری رفیعی بلداجی^۱، محمد رضا یافتیان^۲، حسن شایانی جم^۲

۱. گروه شیمی، دانشگاه پیام نور، صندوق پستی ۳۶۹۷-۱۹۳۹۵، تهران، ایران

۲. گروه شیمی، دانشگاه زنجان، صندوق پستی ۳۸۷۹۱-۴۵۳۷۱، زنجان، ایران

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چکیده

یک حسگر جدید بوپرنورفین (BPR) بر اساس الکتروُد کربن شیشه ای اصلاح شده با پلی پیروُل اوراکسیدایز داپ شده با آنیون بنزن-۱-۳-دی سولفونات بروی نانولوله های کربن چنددیواره ساخته شده است. نانولوله های کربنی بر روی یک الکتروُد برهنه تخلیه و خشک شدند و سپس یک لایه نازک از پلی پیروُل اوراکسیدایز داپ شده با بنزن-۱-۳-دی سولفونات به صورت الکتروشیمیایی روی آن تشکیل شد. اثر شرایط آزمایش شامل pH الکتروولیت حامل، اندازه قطره سوسپانسیون نانولوله های کربنی و تعداد چرخه های پتانسیل در پلیمریزاسیون اضافه اکسید شده با نظارت بر پاسخ های ولتامتری الکتروُد اصلاح شده، بهینه سازی شد. سپس از الکتروُد اصلاح شده بهینه سازی شده برای اندازه گیری الکتروشیمیایی BPR توسط ولتامتری پالس دیفرانسیل استفاده شد که یک رشد خطی با حساسیت بالا در جریان های پیک آندی در محدوده غلظت ۰.۰۶-۴۰ میکرومولار از BPR و حد تشخیص ۲۸ نانومولار نشان داد. سرانجام، اندازه گیری BPR در نمونه های واقعی ادرار توسط حسگر جدید انجام شد و نتایج رضایت بخشی به دست آمد.

واژه های کلیدی

بوپرنورفین، نانولوله های کربن چنددیواره؛ پلی پیروُل اوراکسیدایز؛ نانوکامپوزیت؛ حسگر الکتروشیمیایی؛ ولتامتری پالس تفاضلی.