# Preparation of cobalt oxide/gold nanoparticle modified glassy carbon electrode for electrochemical detection of dopamine

Ceren Kuşçu[1] (ID), K. Volkan Özdokur[2*] (ID), Süleyman Koçak[3] (ID), F. Nil Ertaş[1] (ID)

[1]Ege University, Faculty of Science, Department of Chemistry, İzmir, Turkey
[2]Erzincan Binali Yıldırım University, Faculty of Art & Science, Department of Chemistry, Erzincan, Turkey
[3]Manisa Celal Bayar University, Faculty of Art & Science, Department of Chemistry, Manisa, Turkey

## Abstract

This study deals with electrochemical preparation of cobalt oxide modified glassy carbon electrodes decorated with gold nanoparticles as an effective platform for dopamine (DA) detection. The experimental parameters affecting the oxidation signal of DA by square wave voltammetry have been evaluated. Under optimal conditions, developed sensor exhibited a linear response towards to DA in the concentration range of $6.00 \times 10^{-8}$ to $7.15 \times 10^{-6}$ M. The detection and quantification limits were calculated as $2.0 \times 10^{-8}$ and $6.0 \times 10^{-8}$ M, respectively. The repeatability and reproducibility of the electrode were calculated as 13.2 and 16.1% for $6.5 \times 10^{-7}$ M (N=5), respectively. Finally, the sensor was successfully applied for the DA analysis in artificial cerebrospinal fluid, and the mean recovery was found as 105.8 ±6.5% by the standard addition method.

## 1. Introduction

Dopamine (3,4-dihydroxyphenethylamine, DA) belongs to catecholamine and phenethylamine families. From the chemical point of view, DA is an amine that can be produced by decarboxylation of L-Dopa. DA is an important neurotransmitter and plays a number of significant roles in the human brain and body [1]. It is responsible for communications of nerve cells and plays a major role in reward-motivated behavior [2].

There are several distinct dopamine pathways in our brain and the level and neuronal activity of DA is increased by most reward and addictive drug types, respectively. Other dopamine systems are responsible for motor control and in releasing of other important hormones [3]. On the other hand, an abnormal level of DA has been found related to some neurological disorders such as schizophrenia, Parkinson's and Huntington's diseases [2]. Thus, it is very crucial to detect and quantitate the dopamine in biological samples such as brain fluids, plasma, and urine.

Various analytical methods have been described in the literature including colorimetric and fluorometric methods [4-6], gas chromatography with tandem mass detection [7,8], high performance liquid chromatography coupled with various detectors [9-11], chemiluminescence [12]. These methods, however, have some drawbacks being labor-intensive or time-consuming, and most of them require expensive instrumentation. Electrochemical analysis methods, on the other hand, are very popular since very sensitive and selective methods can be developed at a very low cost. Amperometric [13,14] and voltammetric [15-17] methods have been developed for DA detection in micromolar levels in the presence of ascorbic acid. However, the oxidation peak of the dopamine is prone to the interference of electroactive matrix constituents and therefore, the electrode surfaces have been modified with conductive polymers, carbonaceous materials, conductive polymers, metal nanoparticles, and/or metal oxides.

Recent studies utilize square wave voltammetry for DA detection at carbon-based electrodes including glassy carbon disk modified with reduced graphene oxide for human serum samples [18], nitrogen-doped graphene modified glassy carbon electrode (GCE) [19] or carbon-fiber microelectrodes suitable for in-vivo analysis [20]. Carbon-based electrodes modified with cobalt phthalocyanine complexes have been widely used for the detection of catecholamines but weakly adsorbed complexes suffer from the low conductivity [21]. Carbonaceous nanomaterials, particularly graphenes are often employed as conducting supports on the electrode surfaces for achieving a selective and sensitive DA determination [22, 23].

Metal oxides, on the other hand, are becoming more popular due to their unique electrochemical properties, chemical stability, and low-cost. However, some metal oxides may fail to show the desired catalytic activity and this limitation can be eliminated by decorating the transition metal oxide film with noble metallic nanoparticles. This hyper d-hypo d element combination provides a synergistic effect and enhances the catalytic activity [24].

Among the transition metals, cobalt and its oxide species along with their nanomaterials have drawn a great deal of attention due to their outstanding electronic, optical, magnetic, and catalytic properties [25].

Various types of cobalt oxides with different catalytic performances have been synthesized and used for catalysis and analytical purposes [26].

Their performance is not only dependent on the structure of the cobalt oxide but, also depends on its fabrication process [27, 28]. Electrochemical deposition is probably the best solution for controlling the catalytic properties where the potential is either cycled between two limits suitable for the growth of the metal oxide film or applied in the form of pulses between the limits for certain duration times. The latter technique, also known as the pulsed deposition, results in a more ordered film structure with better catalytic activity in both directions [29].

Here we report a simple, cheap, and green methodology for the synthesis of Au nanoparticles decorated cobalt oxide film for dopamine detection in trace levels. The surface morphology of the electrode was characterized by using Field-Effect Scanning Electron Microscopy (FESEM) and then, the analytical performance of the electrode was investigated. The method was applied to the determination of dopamine at nanomolar levels in artificial cerebrospinal fluid.

## 2. Materials and method

### 2.1. Reagents and apparatus

Analytical grade reagents and ultrapure water obtained from Milli Pore (with 18.2 MΩ resistivity) were used throughout the study. Cobalt (II) chloride hexahydrate, potassium gold (III) chloride, dopamine hydrochloride, ascorbic acid, uric acid, sodium chloride, potassium ferricyanide, potassium ferrocyanide, sodium hydrogen carbonate, potassium chloride, sodium dihydrogen phosphate, magnesium chloride, glucose, calcium chloride, acetic acid, chloroacetic acid, hydrochloric acid, phosphoric acid, boric acid, and sodium hydroxide were purchased from Sigma Aldrich from Germany. Britton Robinson (BR) buffer consisted of 0.08 M acetic, phosphoric, and boric acid each, the final pH was adjusted with 3 M NaOH solution. Chloroacetic acid-acetate buffer solution (CAA-Ac) was prepared from 0.1 M CAA and 0.1 M acetic acid and pH was adjusted to pH 4.0 with 3.0 M NaOH.

Artificial cerebrospinal fluid was prepared by mixing 119 mM NaCl, 26.2 mM NaHCO$_3$, 2.5 mM KCl, 1 mM NaH$_2$PO$_4$, 1.3 mM MgCl$_2$, 10 mM glucose and 2.5 mM CaCl$_2$ dissolved in ultrapure water and stored at 4°C. This solution was stable for 3-4 weeks.

Electrochemical measurements were performed by using Autolab PGSTAT101 (Metrohm, Netherland) voltammetric analyzer with a three-electrode system consisting of Ag/AgCl (sat. KCl) as the reference electrode, Pt wire as the counter electrode and GCE (BASi, 3 mm diameter and a surface area of 0.07 cm$^2$) as the working electrode. The inspection of the modified surfaces was made by using an FEI Quanta 450 FESEM that was used for SEM analysis.

### 2.2. Electrode modification procedure

Prior to each experiment, the GCE was polished with 0.3-micron alumina slurry and treated with water and ethanol mixture in an ultrasonic bath. After rinsing with ultrapure water, the electrode was dipped into a 0.05 M Co(II) solution in pH 4.0 CAA/Acetate buffer. The GCE surfaces have been modified with metal oxide film by cycling the potential in the range of 0.5 - -1.2 V for 5 times at a scan rate of 75 mV s$^{-1}$. Then, the obtained electrode (CoO$_x$/GCE) was immersed into a 1×10$^{-4}$ M Au(II) solution prepared in 0.1 M HCl solution and further deposition was achieved by cycling the potential

between 0.0 and 1.2 V at a rate of 75 mV s$^{-1}$ for 15 times. The electrode obtained by this means was denoted as Au/CoO$_x$/GCE.

### 2.3. Electrochemical measurements

The electrochemical behavior of dopamine (DA) was tested by using voltammetric techniques in the potential range of 0 to 1.0 V at different scan rates. Linear Sweep Voltammetry (LSV), Differential Pulse Voltammetry (DPV), Square Wave Voltammetry (SWV) techniques were utilized for this purpose. Instrumental parameters of SWV were as follows; frequency (*f*) 25 Hz, pulse amplitude (ΔE) 20 mV, and staircase step (ΔEs) 5 mV and the potential between 0.00 and 1.00 V. Efficient Surface Area (ESA) calculation was made from the cyclic voltammetric measurements carried out in 2.5×10$^{-3}$ M K$_3$[Fe(CN)$_6$] and K$_4$[Fe(CN)$_6$] solution containing 0.1 M KCl.

## 3. Results and discussion

### 3.1. Characterization

The inspection of the surface morphology of the modified electrode was made by the FESEM measurements along with the Energy Dispersive Spectroscopy (EDAX) spectra. A smooth surface of the bare GCE was clearly seen in Fig. 1A. After the modification with CoO$_x$ on GCE, irregular spherical deposits were observed in the range of 70-100 nm and the chemical composition of the deposit was proven with the EDAX results (Fig. 1B). Fig. 1C depicted the closer image of Au/CoO$_x$/GCE and the Au nanoparticles were about 70 nm-sized and homogenously distributed onto the CoO$_x$/GCE surface.
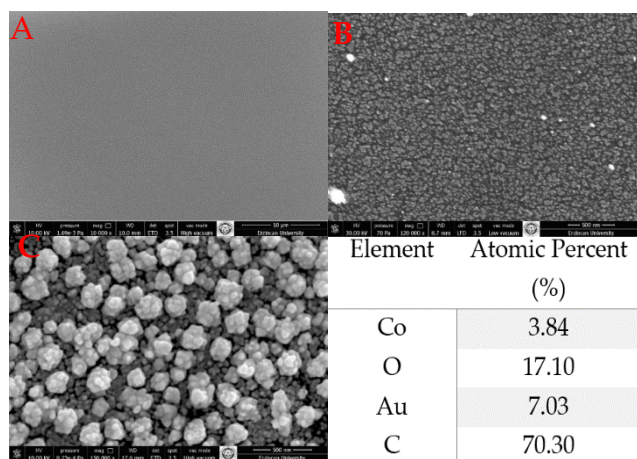


| Element | Atomic Percent (%) |
|---|---|
| Co | 3.84 |
| O | 17.10 |
| Au | 7.03 |
| C | 70.30 |

**Figure 1.** SEM images of A) Bare GCE, B) CoO$_x$ /GCE, C) Au/CoO$_x$/GCE electrode and EDAX result of Au/CoO$_x$/GCE electrode.

The electrochemical characterization of the modified surfaces was accomplished by recording the cyclic voltammograms. A linear correlation was observed between anodic peak current observed for 2.5 mM K$_3$Fe(CN)$_6$ and K$_4$Fe(CN)$_6$ solution and the square root of the scan rate, indicating the diffusion-controlled electrode process (Supplementary Figure 1). The electroactive surface area (ESA) is calculated by applying the data obtained above to the Randles-Sevcik equation (Eq. 1).

$$I_p = (2.69 \times 10^5)n^{3/2}AD^{1/2}C^*v^{1/2} \qquad (1)$$

Here; $I_P$ is the anodic peak current of ferrocyanide, n is the numbers of the electron processed in redox reaction (n=1), $A$ is the electroactive surface area (cm$^2$), $D$ is the diffusion coefficient (6.7×10$^{-6}$ cm$^2$ s$^{-1}$ at 25°C), $C^*$ is the concentration of K$_3$Fe(CN)$_6$ (2.5 mM) and ν is scan rate of potential scan (V s$^{-1}$) [30]. The ESA of GCE, CoO$_x$/GCE, and Au/CoO$_x$/GCE were calculated as 0.05, 0.08, 0.13 cm$^2$, respectively.

### 3.2. Electrochemical behavior of DA

After the characterization of the Au/CoO$_x$/GCE electrode, well-known voltammetric techniques have been applied for revealing the electrochemical behavior of DA. CV, LSV, DPV, and SWV measurements recorded in 6.52×10$^{-6}$ M DA in pH 2.00 BR buffer and on the basis of the current signal, the SWV has resulted in the most sensitive results (Data not have shown). Therefore, further experiments were performed with the SWV technique while the CV was utilized for the optimization studies.

The comparison of step-by-step modified electrodes is given in Fig. 2. DA has displayed an oxidation peak at 0.57 V with a peak current of 7.0 μA on the bare GCE surface. After the modification with CoO$_x$ (CoO$_x$/GCE), DA peak was shifted to 0.51 V and the peak current has arisen to 10.3 μA. Further decoration with AuNP (Au/CoO$_x$/GCE) has led to a 30 mV potential shift to the negative direction while the peak current has increased to 21.0 μA. Gold nanoparticles decorated bare GCE (Au/GCE) were also prepared for comparison, and this electrode has exhibited an oxidation peak at 0.53 V with a peak current of 13.0 μA. The enhancement in the peak current can be attributed to the synergistic effect between CoO$_x$ and AuNP due to the hyper d-hypo d attraction.

### 3.3. Electrochemical characterization of DA and optimization studies

The effects of the experimental parameters on the DA signal were investigated by using $6.52 \times 10^{-6}$ M DA. The initial parameter was chosen the pH of the electrochemical cell and this parameter was studied in the pH range of 2.0 - 11.0 by using BR buffer.
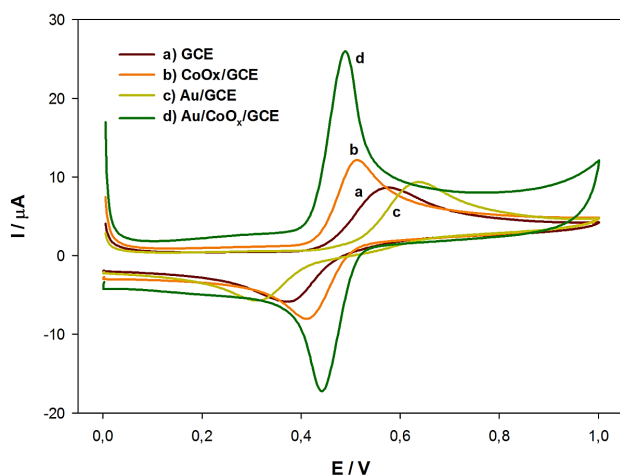


**Figure 2** The comparative CV voltammograms of step-by-step modified electrodes for $6.52 \times 10^{-6}$ M DA in pH 2.0 BR buffer.

The results were given in Fig. 3. The anodic peak current of DA was increased by increasing pH up to 6.0, after this pH the anodic peak current was diminished. The optimum pH was designated as 6.0 and used for further studies. On the other hand, the oxidation peak potential ($E_{ox}$) has shifted to a negative direction with increasing medium pH, meaning the hydronium ion has participated in the electrochemical process.
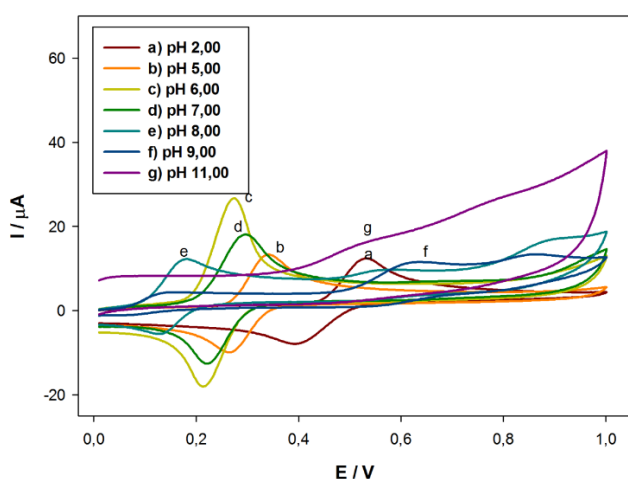


**Figure 3.** Effect of measurement medium pH on $6.52 \times 10^{-6}$ M DA signal.

The relation between pH and $E_{ox}$ was found linear with an equation of $E_P = -0.063$ pH $+ 0.6548$ in the range of 2 to 8. The slope of the pH curve is close to the identical value of 0.059 V, indicating the equal

number of protons and electron transferred in the electrochemical process [31]. Further electrochemical information for the DA oxidation mechanism was obtained by changing the CV scan rate in the range of 5 to 1000 mV s$^{-1}$. The relationship between oxidation peak current ($I_{pa}$) of $6.52 \times 10^{-6}$ M mol L$^{-1}$ DA and the square root of the scan rate ($v^{1/2}$) was found linear with an equation of $I_{pa}= 3.657$ (SR)$^{1/2}$ - 8.07 and correlation coefficient of (R$^2$) 0.9901. These results were indicating that mass transportation was controlled by diffusion.

The thickness of the deposits grown on the electrode is generally related to the cell concentration of precursor ions, deposition cycle numbers, and scan rate. Accordingly, Co(II) concentration was varied between 0.005 - 0.5 M and 0.05 M was found as an optimal value (Supplementary Figure 2). Another parameter is the deposition scan rate applied during the CoOx deposition. The scan rate was changed between 5 to 100 mV s$^{-1}$ and 75 mV s$^{-1}$ was given the best result (Supplementary Figure 3). Finally, the repetitive cycle number is another important parameter to film growth, and therefore the thickness can be controlled by changing this parameter. Repetitive cycle number was started from 2 and increased up to 40 cycles and the voltammograms have revealed that the oxidation peak current of DA has given a maximum at 5 cycles, after this value the oxidation peak current has reached a plateau (Supplementary Figure 4). Therefore, consecutive five cycles were used for further studies. Similar parameters were investigated for Au nanoparticle deposition and overall results were summarized in Table 1.

**Table 1. Optimal condition for CV deposition of CoOx and Au.**

| Parameter | | Range | Optimum value |
|---|---|---|---|
| Cell Conc. (M) | Co (II) | 0.005 - 0.5 | 0.05 |
| | AuCl$_4^-$ | - | 0.0001 |
| Scan rate (mV s$^{-1}$) | CoOx | 5 - 100 | 75 |
| | AuNP | 5 - 100 | 75 |
| Cycle number | CoOx | 2 - 40 | 5 |
| | AuNP | 2 - 20 | 15 |

### 3.4. Analytical characteristics of the method

After the characterization of the modified surface characteristics and electrochemical process of DA, the analytical performance of the developed surfaces was tested. Au/CoOx/GCE electrode was exhibited linear response in the concentration range of $6.0 \times 10^{-8}$ to $7.15 \times 10^{-6}$ M DA. The SWV voltammograms and the calibration curve were given Fig. 4 and the linear equation was calculated as $I_P = 526258$ C$_{DA} + 0.303$ with a correlation coefficient (R$^2$) of 0.9983.

Signal to noise (S/N) was set to three for the limit of detection (LOD) and five for the limit of quantification (LOQ) and these values were calculated as 20 and 60 nM, respectively. The repeatability (interday, N=5) and reproducibility (intraday, N=5) were determined as relative standard deviation (RSD) and figured out as 13.2 and 16.1% for $6.5 \times 10^{-7}$ M, respectively.
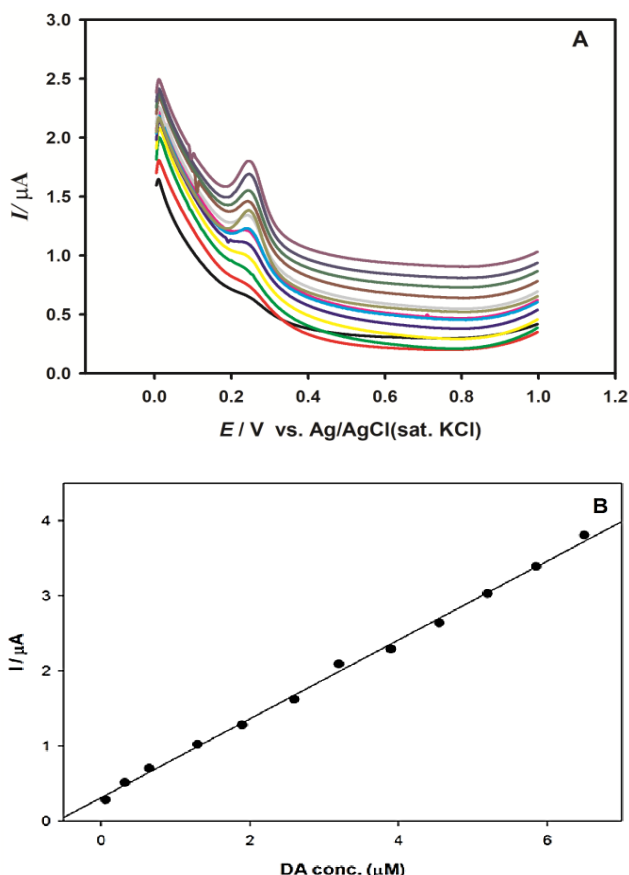


**Figure 4.** SWV voltammograms of $6.0 \times 10^{-8}$ to $7.15 \times 10^{-6}$ M dopamine and the calibration curve.

The accuracy of the calibration curve was tested by analyzing quality control samples with a concentration of $6.5 \times 10^{-7}$ M and the recovery of the sample was found as 107.3% for this concentration. The possible interference of 1.0 mM of NaCl, $NaHCO_3$, KCl, $NaH_2PO_4$, $MgCl_2$, glucose, $CaCl_2$, $50.0 \times 10^{-6}$ M ascorbic acid, and uric acid was tested. No interference was observed for the $6.5 \times 10^{-7}$ M DA signal. The stability of the electrode was tested by analyzing $6.5 \times 10^{-7}$ M DA, and the electrode developed was shown 98% of its initial activity after 50 measurements. The method developed was applied to DA analysis in ACSF by the standard addition method. A satisfactory recovery value (105.8±6.5%) was obtained for $6.5 \times 10^{-7}$ M DA in ACSF.

The developed sensor performance was compared with the literature studies in Table 2. According to the literature survey, the sensor developed is a good candidate for the trace analysis of DA. The analytical characteristics of the developed sensor were found comparable with the literature in terms of detection limit and linear range.

**Table 2.** Comparison of AuNPs/CoOx/GCE analytical performance with previous reported electrochemical methods.

| Electrode | Technique | Linear Range (μM) | LOD (μM) | Ref. |
|---|---|---|---|---|
| BCNTs/GCE | DPV | 0.02 - 75.00 | 0.001 | [32] |
| Gr/AuNPs/GCE/ | DPV | 5.0 - 1000 | 1.860 | [33] |
| AuNPs/Ch/GCE/ | DPV | 0.2 - 80 | 0.120 | [34] |
| Gr/Pt/GCE | Amperometry | 0.03-8.13 | 0.030 | [35] |
| RGO-Pd/GCE | LSV | 1-150 | 0.230 | [36] |
| Methylene blue/ MWCNT/GCE | DPASV | 0.4-10 | 0.200 | [37] |
| AuNPs/CoOx/GCE | SWV | 0.06 - 7.15 | 0.020 | This study |

(BCNTs: Boron-doped carbon nanotubes, AuNPs: Gold nanoparticles, Gr: Graphene, Ch: Choline, CoOx: Cobalt oxide, MWCNT: multi-walled carbon nanotube, Pt: Platinum, RGO: reduced graphene oxide, Pd: Palladium, DPV: Differential pulse voltammetry, LSV: Linear scan voltammetry, DPASV: Differential pulse anodic stripping voltammetry, SWV: Square wave voltammetry)

## 4. Conclusion

The present study reported, metal/metal oxide modified electrode for sensitive DA analysis. Au/CoOx/GCE/ electrode was prepared via CV technique and characterized by various methods. Au/CoOx/GCE electrode exhibited a catalytic signal towards DA oxidation. Three-fold current enhancement was obtained while the peak potential shifted 100 mV negative to the negative direction. The synergetic effect between CoOx and AuNP is responsible for the current enhancement due to the hyper-hypo d attraction. The analytical characteristics were found comparable with the literature values.

## References

[1] G. Di Chiara, V. Bassareo, Reward system and addiction: What dopamine does and doesn't do, Curr Opin Pharmacol, 7, 2007, 69-76.

[2] D. Meder, D.M. Herz, J.B. Rowe, S. Lehericy, H.R. Siebner, The role of dopamine in the brain - lessons learned from Parkinson's disease, Neuroimage, 190, 2019, 79-93.

[3] A. Bjorklund, S.B. Dunnett, Dopamine neuron systems in the brain: An update, Trends Neurosci, 30, 2007, 194-202.

[4] J. Wang, R. Du, W. Liu, L. Yao, F. Ding, P. Zou, Y. Wang, X. Wang, Q. Zhao, H. Rao, Colorimetric and fluorometric dual-signal determination of dopamine by the use of Cu-Mn-O

microcrystals and C dots. Sensor Actuat B: Chem, 290, 2019, 125-132.

[5] Y. Tao, Y. Lin, J. Ren, X. Qu, A dual fluorometric and colorimetric sensor for dopamine based on BSA-stabilized Au nano clusters, Biosens Bioelectron, 42, 2013, 41-46.

[6] S. Roastami, A. Mehdinia, A. Jabbari, E. Kowsari, R. Niroumand, T.J. Booth, Colorimetric sensing of dopamine using hexagonal silver nanoparticles decorated by task-specific pyridinum based ionic liquid, Sensor Actuat B: Chem, 271, 2018, 64-72.

[7] A. Naccarato, E. Gionfriddo, G. Sindona, A. Tagaralli, Development of a simple and rapid solid phase microextraction-gas chromatography-triple quadrupole mass spectrometry method for the analysis of dopamine, serotonin and norepinephrine in human urine, Anal Chim Acta, 810, 2014, 17-24.

[8] F. Musshoff, P. Schmidt, R. Dettmeyer, F. Priemer, K. Jachau, B. Madea, Determination of dopamine and dopamine-derived (R)-/(S) salsolinol and norsalinol in various human brain areas using solid-phase extraction and gas chromatography/mass spectrometry, Forensic Sci Int, 113, 2000, 359-366.

[9] A. Gottås, Å. Ripel, F. Boix, V. Vindenes, J. Mørland, E.L. Øiestad, Determination of dopamine concentrations in brain extracellular fluid using microdialysis with short sampling intervals, analyzed by ultrahigh performance liquid chromatography tandem mass spectrometry, J Pharmacol Tox Met, 74, 2015,75-79.

[10] M. Oh, E. Huh, M.S. Oh, J. Jeong, S. Hon, Development of a diagnostic method for Parkinson's disease by reverse-phase high-performance liquid chromatography coupled with integrated pulsed amperometric detection, J Pharmaceut Biomed Analysis, 153, 2018, 110-116.

[11] L. Dillen, M. Claeys, W.P.D. Potter, Determination of dopamine-β- hydroxylase in cerebrospinal fluid by high-performance liquid chromatography with electrochemical detection, J Pharmacol, 15, 1986, 51-63.

[12] W. Gao, L. Qi, Z. Liu, S. Majeed, S. A. Kitte, G. Xu, Efficient lucigenin/thiourea dioxide chemiluminescence system and its application for selective and sensitive dopamine detection, Sensor Actuat B, 238, 2017, 468-472.

[13] K. Min, Y.J. Yoo, Amperometric detection of dopamine based on tyrosinase-SWNTs-Ppy composite electrode, Talanta, 80, 2009, 1007-1011.

[14] H. Duan, L. Li, X. Wang, Y. Wang, J. Li, C. Luo, A sensitive and selective chemiluminescence sensor for the determination of dopamine based on silanized magnetic graphene oxide-molecularly imprinted polymer, Spectrochim Acta A, 139, 2015, 374-379.

[15] W.-L. Yeh, Y.-R. Kuo, S.-H. Cheng, Voltammetry and flow-injection amperometry for indirect determination of dopamine, Electrochem Commun, 10, 2008, 66-70.

[16] L. Zhang, T. Norio T., Hasebe, M. Kurihara, T. Kawashima, Flow-injection determination of trace amounts of dopamine by chemiluminescence detection, Talanta, 50, 1999, 677-683.

[17] Y. Sun, Y. Lin, C. Ding, W. Sun, Y. Dai, X. Zhu, H. Liu, C. Luo, An ultrasensitive and ultraselective chemiluminescence aptasensor for dopamine detection based on aptamers modified magnetic mesoporous silica @ graphite oxide polymers, Sensor Actuat B: Chem, 257, 2018, 312-323.

[18] A.M. Granero, G.D. Pierini, S.N. Robledo, M.S. Di Nezio, H. Fernández, Zon, M.A. Simultaneous determination of ascorbic and uric acids and dopamine in human serum samples using three-way calibration with data from square wave voltammetry, Microchem J, 129, 2016, 205-212.

[19] A. Hatefi-Mehrjardi, A. Beheshti-Marnani, N. Askari, Cu$^{+2}$ loaded "zeolite A"/ nitrogen-doped graphene as a novel

hybrid for simultaneous voltammetry determination of carbamazepine and dopamine, Mater Chem Phy, 225, 2019, 137-144.

[20] Y. Oh, M.L. Heien, C. Park, Y.M. Kang, J. Kim, S.L. Boschen, H. Shin, H.U, Cho, C.D. Blaha, K.E. Bennet, H.K. Lee, S.J. Jung, I.Y. Kim, K.H. Lee, D.P. Jang, Tracking tonic dopamine levels in vivo using multiple cyclic square wave voltammetry, Biosens Bioelectron, 121, 2018, 174-182.

[21] J.H. Zagal, S. Griveau, J.F. Silva, T. Nyokong, F. Bedioui, Metallophthalocyanine-based molecular materials as catalysts for electrochemical reactions, Coordin Chem Rev, 254, 2010, 2755-2791.

[22] J. Yang, D. Mu, Y. Gao, J. Tan, A. Lu, D. Ma, Cobalt phthalocyanine-graphene complex for electro-catalytic oxidation of dopamine, J Nat Gas Chem, 21, 2012, 265-269.

[23] N. Diab, D.M. Morales, C. Andronescu, M. Masoud, W. Schuhmann, A sensitive and selective graphene/cobalt tetrasulfonated phthalocyanine sensor for detection of dopamine, Sensor Actuat B: Chem, 285, 2019, 17-23.

[24] K.V. Özdokur, S. Koçak, F.N. Ertaş, Nanostructures Metal-Metal oxides and Their Electrocatalytic Applications. Chapter in Advanced coating Materials, Editors: L. Li, Q. Yang, 2019, Wiley Interscience.

[25] Q. Wang, W. Hu, Y. Huang, Nitrogen doped graphene anchored cobalt oxides efficiently bi-functionally catalyze both oxygen reduction reaction and oxygen revolution reaction, Int J Hydrogen Energ, 4, 2017, 5899-5907.

[26] I.G. Casella, M. Contursi, Cobalt oxide electrodeposition on various electrode substrates from alkaline medium containing Co-gluconate complexes: A comparative voltammetric study, J Solid State Electr, 1, 2012, 3739-3746.

[27] R. Hallaj, K. Akhtari, A. Salimi, S. Soltanian, Controlling of morphology and electrocatalytic properties of cobalt oxide nanostructures prepared by potentiodynamic deposition method, Appl Surf Sci, 276, 2013, 512-520.

[28] C. Kuşçu, K.V. Özdokur, S. Koçak, F.N. Ertaş, Development of cobalt oxide film modified electrode decorated with platinum nanoparticles as a biosensing platform for phenol, Int J Environ An Ch, 14, 2019, 1-7.

[29] K.V. Özdokur, A.Y. Tatlı, B. Yılmaz, S. Kocak, F.N. Ertaş, Development of pulse deposited manganese and molybdenum oxide surfaces decorated with platinum nanoparticles and their catalytic application for formaldehyde oxidation, Int J Hydrogen Energ, 41, 2016, 5927-5933.

[30] Ç.C. Koçak, Poly(taurine-glutathione)/carbon nanotube modified glassy carbon electrode as a new levofloxacin sensor, Electroanal, 31(8), 2019, 153-1544.

[31] Ş. Ulubay, Z. Dursun, Cu nanoparticles incorporated polypyrrole modified GCE for sensitive simultaneous determination of dopamine and uric acid, Talanta, 80(3), 2010, 1461-1466.

[32] C. Deng, J. Chen, M. Wang, C. Xiao, Z. Nie, S. Yao, A novel and simple strategy for selective and sensitive determination of dopamine based on the boron-doped carbon nanotubes modified electrode, Biosens Bioelectron, 24, 2009, 2091-2094.

[33] J. Li, J. Yang, Z. Yang, Y. Li, S. Yu, Q. Xu, X. Hu, Graphene-Au nanoparticles nanocomposite film for selective electrochemical determination of dopamine, Anal Methods, 4, 2012, 1725-1728.

[34] P. Wang, Y. Li, X. Huang, L. Wang, Fabrication of layer-by-layer modified multilayer films containing choline and gold nanoparticles and its sensing application for electrochemical determination of dopamine and uric acid, Talanta, 73, 2007, 431-437.

[35] C.L. Sun, H.-H. Lee, J.-M. Yang, C.-C. Wu, The simultaneous electrochemical detection of ascorbic acid, dopamine, and uric acid using graphene/size-selected Pt nanocomposites, Biosens Bioelectron, 26, 2011, 3450-3455.

[36] S. Palanisamy, S. Ku, S.-M. Chen, Dopamine sensor based on a glassy carbon electrode modified with a reduced graphene oxide and palladium nanoparticles composite, Microchim Acta, 180, 2013, 1037-1042.

[37] S.L. Yang, G. Li, R. Yang, M.M. Xia, Qu, L.B. Simultaneous voltammetric detection of dopamine and uric acid in the presence of high concentration of ascorbic acid using multi-walled carbon nanotubes with methylene blue composite film-modified electrode, J Solid State Electr, 15, 2011, 1909-1918.