ISSN: 2578-7365

Research Article

Journal of Chemistry: Education Research and Practice

Electrochemical Biosensor Based on Furosemide-Gold Nanoparticles for The Determination of Dopamine for Practical Applications

Maqsood Ahmed Abro[1], Farman Ali Mangi[1], Deedar Ali Jamro[1], Naimatullah Channa[4], Ihsan Ali Mallah, Sikander Ali Larik[1], Sajid Hussain Metlo[5], Mansib Ali Jakhrani[1], Dost Mohammad Kalhoro[3], Aijaz Ali Otho[3] & Abdul Qayoom Mugheri[2*]

[1]*Department of Physics and Electronics Shah Abdul Latif University Khairpur Sindh, Pakistan*

[2]*Dr. M.A Kazi Institute of Chemistry University of Sindh Jamshoro, 76080, Sindh Pakistan*

[3]*Institute of plant sciences University of Sindh, Jamshoro, 76080 Sindh Pakistan*

[4]*Beijing university of Engineering of chemical technology, Beijing china*

[5]*College of nuclear science and technology Harbin engineering university of china*

[*]Corresponding author
Abdul Qayoom Mugheri, Dr. M.A Kazi Institute of Chemistry University of Sindh Jamshoro, 76080, Sindh Pakistan

Submitted: 11 Jan 2021; **Accepted**: 18 Jan 2021; **Published**: 01 Feb 2021

Citation: *Maqsood Ahmed Abro, Farman Ali Mangi, Deedar Ali Jamro, Naimatullah Channa, Ashan Ali Mallah, Sikander Ali Larik, Sajid Ali Metlo, Mansib Ali Jakhrani, Sajid Hussain, Dost Mohammad Kalhoro, Aijaz Ali Otho & Abdul Qayoom Mugheri (2021) Electrochemical Biosensor Based on Furosemide-Gold Nanoparticles for The Determination of Dopamine for Practical Applications. J Chem Edu Res Prac 5: 36-41.*

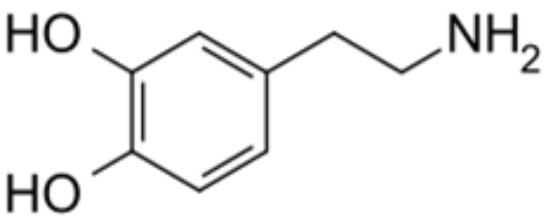
Abstract

In this study, by taking the advantage of the facile & controlled synthesis of furosemide derived gold nanoparticles (Fr-AuNps) for rapid and sensitive amperometric determination of dopamine (DP). The one-step synthesis of Fr-AuNps was carried out at room temperature without the use of strong reducing agents. The synthesized Fr-AuNps were studied by UV-Vis spectroscopy, and a strong absorption band for gold nanoparticles was observed at 520 nm. Transmission electron micrographs (TEM) revealed the average particle size below 100 nm. HRTEM showed excellent crystalline features as prepared gold nanoparticles. The electrochemical behavior of gold nanoparticles was examined by cyclic voltammetry (CV) which demonstrated the enhanced electrocatalytic kinetics activity towards the oxidation of dopamine. The presented dopamine biosensor exhibited a linear response for the dopamine in the range of 0.25 to 7 µM. The calculated the detection limit found to be 18.3 nM and limit of quantification 61.5 nM respectively. The proposed dopamine biosensor was successfully employed for the quantification of trace amount of dopamine from human serum and the obtained results are very satisfactory.

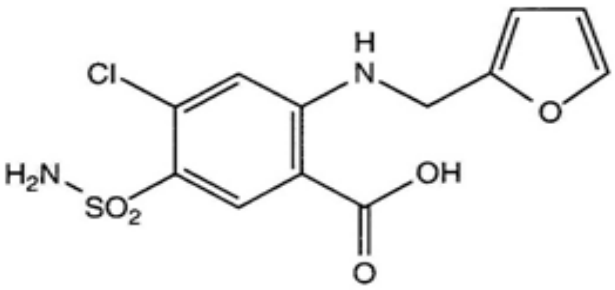
Keywords: Furosemide, Gold Nanoparticles, Cyclic Voltammetry, Amperometry, Dopamine

Introduction

Dopamine (DP) is an endogenous catecholamine present in the human body that plays a fundamental role in proper functioning of the central nervous system, renal, hormonal & cardiovascular systems [1]. Depressed levels of dopamine in substantia nigra of brain that may lead to motor system abnormality known as Parkinson's disease, whereas the elevated levels of dopamine clinically manifest as schizophrenia [2,3]. Development of methods for the determination of dopamine in human blood is captivating extensive interest due to its clinical implications [4,5]. Owing to its facile oxidation at the electrode surface, electroanalysis has proved to be the method of the best choice for the quantitative determination of dopamine in physiological fluids [6,7]. Various electrochemical methods have been reported for the analysis of DP employing modified electrodes such as polymer matrix, metal nanoparticles, oxide nanoparticles, carbon nanotubes and so forth [8-12]. Among metal nanoparticles gold nanoparticles (AuNps) have found considerable interest in the fabrication of modified electrodes for the determination of biomolecules due to their biocompatible nature [13,14]. Numerous methodologies have been devised by modifying the electrode sensing interface by AuNps nanocomposites for the determination of dopamine in the existence of uric acid & ascorbic acid which usually cause interference in the determination of dopamine [15].



Dopamine



Furosemide

Schematic 1

This work reports the novel strategy for the synthesis of AuNps employing a diuretic drug furosemide as reducing and capping agent. These Fr-AuNps were deposited on the glassy carbon electrode to fabricate sensitive and selective sensor for the determination of DP. Furthermore, nafion a cation exchange ionomer has been utilized to preconcentrate the DP molecules at the Fr-AuNps modified GCE surface and to repel negatively charged interfering species11. The modified sensing platform demonstrates strong electrocatalytic response for the dopamine oxidation. The fabricated biosensor remained employed for the determination of DP in the serum of human samples using hydrodynamic amperometry. This sensor was also tested for its selectivity towards the oxidation of DP in the presence of ascorbic acid & uric acid.

Experimental

Chemicals and Reagents

In this study Choroauric acids (HAuCl4), furosemide (FR), Dopamine (DP), uric acid (UA), ascorbic acid (AA), nafion were obtained from Sigma Aldrich. A stock solution of FR was prepared in methanol while a solution of nafion (0.1%) was prepared in 2-propanol. Different PH buffer of Phosphate buffer solution used and prepared an appropriate amount of 0.1M Na2HPO4 & 0.1MNaH2PO4. Millipore water was used throughout the experiment.

The Synthesis of Fr-AuNps

The synthesis of Fr-AuNps was achieved in aqueous media by addition of 200 µl of 0.2 M NaOH solution and sequential addition of 300 µl each of 0.01M furosemide solution and 0.01M of HAuCl4 solution and the final volume was adjusted to 10 ml with Millipore water. The resultant solution having pH 11.5 was left at room temperature for 15 min till the colour of solution turns wine red indicating the formation of AuNps.

The TEM & HRTEM

For recording TEM images 20 µl of the aqueous Fr-AuNps solution was dried over the copper grid and subjected to TEM investigation. A similar procedure was adopted for sample preparation of HRTEM.

Instrumentation

Fr-AuNps were characterized by UV–Vis spectrophotometer, lambda 25 of Perkin Elmer. TEM was used to disclose the crystalline quality of prepared gold nanoparticles and HRTEM was also employed to get a crystal pattern of gold nanoparticles. Cyclic voltammetry and amperometric measurements and experimental step up were performed (CH Instruments (Texas) USA 700 model).

Fabrication of Electrode with Nanocomposite (Fr-AuNps)

The modification of electrode was mechanically polished to a mirror finish surface with 0.05 µm alumina powder accompanied by sonication in Millipore water and dried under N2 stream. Drop cast method was adopted to modify the conducting surface of GCE [16]. Briefly, 15µL of the was positioned over the surface of GCE and dried at room temperature in order to form a thin film to acquire Fr-AuNps/GCE. Subsequently, a 5 µL drop of 0.1% Nafion was also deposited over Fr-AuNps/GCE to form Nafion/Fr-AuNps/GCE. The purpose of nafion is to prevent the loss of material from the surface of the electrode.

Electrochemical Measurements

The electrochemical experiments were performed in the presence of three electrodes set up system, using the Pt wire was used as a counter electrode, saturated calomel the electrode used a reference electrode & Fr-AuNps/GCE or glassy carbon the electrode used as a working electrode. Cyclic voltammetric studies were carried out in 0.1 M buffer solution of phosphate at pH 7.4 and 0.5 mM dopamine concentration in the applied potential range of -0.20 V to +0.80 V. Amperometric all experiments performed at 0.5V applied potential with further addition of 25 µL of 0.1 mM dopamine solution.

Dopamine Determination in Serum Samples

The proposed dopamine biosensor was significantly employed for the determination of dopamine in human serum by using amperometry mode for analysis of samples. The serum samples were diluted many times with phosphate buffer solution at a constant pH 7.4 & tests of recovery were performed by spiking the standard dopamine solution in the diluted serum contained in an electrochemical cell under stirring.

Results and Discussions

The Characterization of Fr-AuNps by Uv-Vis Spectroscopy, TEM and HRTEM

The synthesis of Fr-AuNps was accomplished in alkaline pH in order to accelerate the process of the formation of AuNps as cited elsewhere [16]. The pH of the solution mixture, concentrations of HAuCl4 and furosemide solutions were optimized in order to explore the blue-shifted absorption band distinctive to AuNps at 520 nm as depicted in Figure 1A. The size and morphological features of the synthesized Fr-AuNps were investigated by TEM which clearly indicates the synthesized particles are spherical in shape and the average size of the particles was found to be less than 100 nm as depicted in Figure 1B. The HRTEM revealed the single crystalline nature of as-prepared gold nanoparticles as shown in Figure 1C, and corresponding SAED image is shown in inset if Figure 1C.

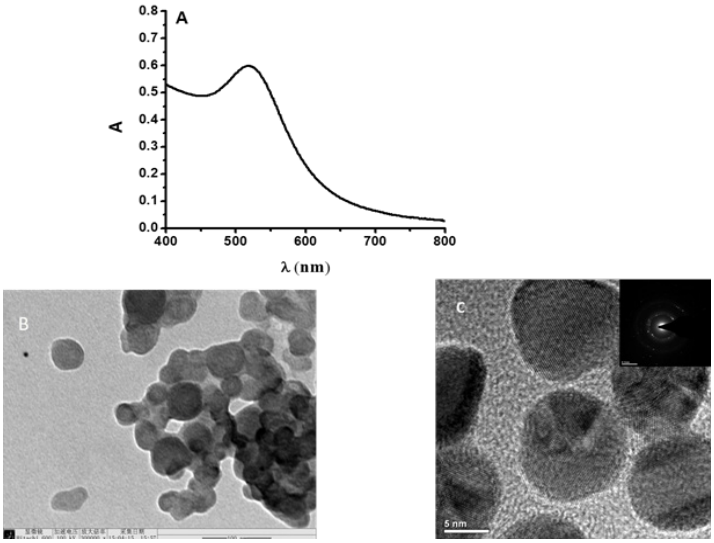


Figure 1: (A) UV-Vis spectra of Fr-AuNps (B) TEM less than 100 nm (C) SAED image

The Electrochemical Response of DP at Fr-AuNps Modified Electrode

The electrochemical behaviour of DP was examined using CV in 0.10 M buffer solution at pH 7.4 which contained 0.5 mM concentration of dopamine at bare GCE, Fr-AuNps/GCE and Nafion/Fr-AuNps/GCE. As depicted in Figure 2 a well-defined anodic peak was perceived in the forward scan at 0.24 V (Epa) with a weak cathodic peak at 0.06V (Epc) at bare GCE. At fr-AuNps/GCE a slight increase in peak current (Ipa and Ipc) was observed while more enhanced peak currents values were observed at nafion/Fr-AuNps/GCE. The oxidation potential values to be shifted to so fewer positive values at both modified GCE with a potential difference of 0.07 V that clearly indicates the electrocatalytic nature of Fr-AuNps. The negatively charged sulfonate groups of nafion impart selectivity towards DP by repelling negatively charged interfering species such as AA and UA but also assist to concentrate DP at the electrode surface by electrostatic interactions [11]. The CV curves were recorded at nafion/Fr-AuNps/GCE by varying scan rates at pH 7.4 at 0.5 mM concentration of dopamine. The anodic and cathodic Ip values were observed to increase with the increase in scan rate range of 0.01 mVs-1 to 1 mV s-1 (Figure 3). An Ip versus square root plot of scan rate that follows a linear relationship and the correlation-coefficient was found to be 0.991, indicating the oxidation of DP tracks a diffusion-controlled electrochemical development the potential difference b/w Epa & Epc also increase with an increase in scan rate [1].

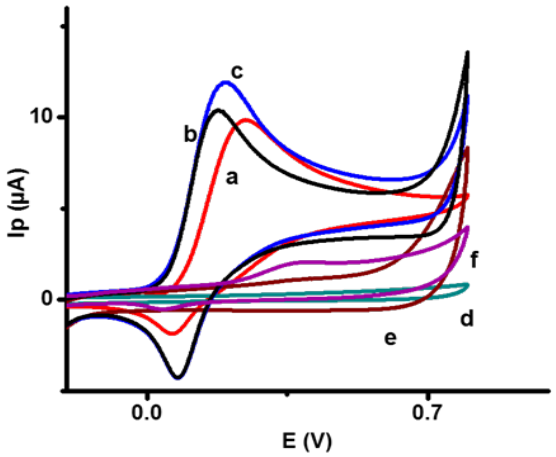


Figure 2: CV of 0.5mM dopamine (a) bare GCE, (b) Fr-AuNps/GCE (c) Fr-AuNps (d) (e) (f) corresponds to respective blanks scan rate 0.05mVs^{-1}

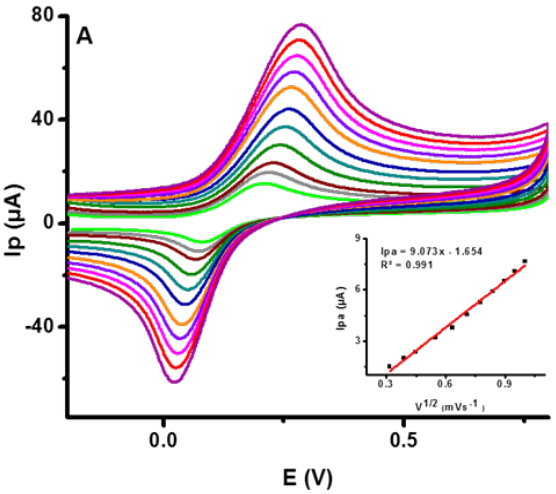


Figure 3: (A) CV of 0.5mM dopamine Fr-AuNps/GCE with different scan rates 100,150,200,300,400,500, 600, 700,800,900 and 1000 mVs-1 (B) plot of Ipa versus square root of scan rate.

An Amperometric Study of Fabricated Dopamine Sensor for The Determination of Dopamine

The response of nafion/Fr-AuNps/GCE for the amount a quantification of dopamine was investigated by recording amperometric current- time detection response curves in 0.1M buffer solution at pH 7.4 under stirred settings at 0.5 V. Figure 4A shows the current-time response curves for the successive additions of 25 µl of DP to the PBS. A visible enhancement in the Ipa was evidenced for each addition of DP. A linear calibration plot (Figure 4B) was generated for the concentration of DP versus Ipa values and the linear regression equation were calculated as Ip = 0.2132x + 0.3247 & correlation coefficient as 0.997. The detection of the limit was calculated by taking III times the standard deviation of blank & divide it by slope value as described in our previous work [16].

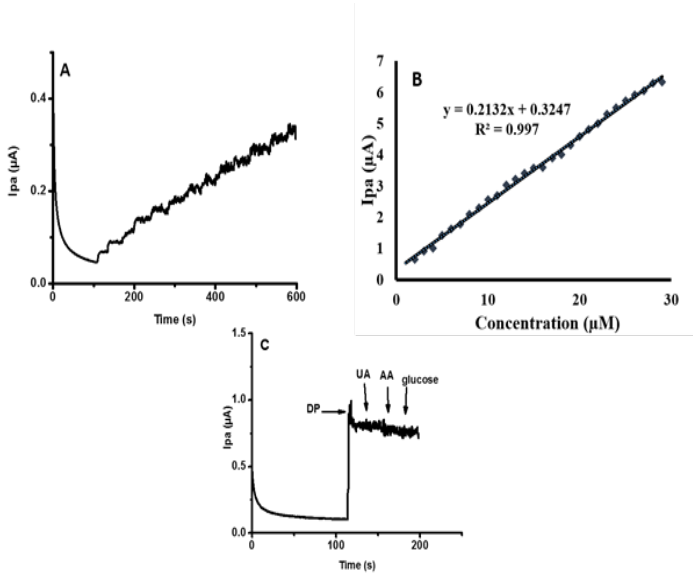


Figure 4: (A) An Amperometric current curves for the successive addition of dopamine solution at applied potential of 0.5 V.(B) calibration plot for peak current on dopamine concentration.(C) Amperometric current response curves for the 1 mM each of AA, UA and glucose in the presence of 1mM DP under stirred conditions.

The Interference Studies

The interference due to endogenous substances is one of the significant issues that affects sensor performance in real samples. Therefore, the amperometric current- time response curves were recorded with 1mM DP concentration in the existence of 1 mM each of AA, UA and glucose at nafion/Fr-AuNps/GCE as depicted in Figure 4C. The well-defined current response was acquired upon the addition of DP while weak signals were obtained by addition of interfering species that demonstrates the excellent applicability of the fabricated sensor with the co-existence of interfering species.

An Application of The Fabricated Biosensor to Serum of Human Samples Analysis

The proposed dopamine biosensor remained evaluated by recording current time response curves in human serum samples. Recovery tests were executed in stirred PBS by first adding diluted serum samples and then successful addition of DP standard to the electrochemical cell. Table 1 shows the results of recovery tests conducted for human serum samples for DP detection. % recovery values were observed in the range of 95 % to 102.6 % for triplicate measurements. Table 2 represents the comparison of the analytical parameters of presented work with the reported works for the determination of DP. It is clearly shown that the proposed biosensor offers enhanced sensitivity and selectivity towards DP with a low limit of detection. This improved performance of the fabricated biosensor in the present study is attributed to the tailored and enhanced electrocatalytic properties of furosemide drug stabilized gold nanoparticles.

Table 1: The content of dopamine in human serum

Samples	Added	Found	Recovery (%)	RSD (%)
Serum 1	-	0.25	-	-
	0.5	0.77	102.6	3.2
Serum 2	-	0.35	-	
	0.5	0.79	92.9	2.1
Serum 3	-	0.11	-	-
	0.5	0.58	95	3.8

Table 2: Comparison of the proposed work biosensor with other reported dopamine sensors

Electrode	Method	Linear range (µM)	Limit of detection (LOD)µM	Reference
AuNps immobilized on amine terminated SAM on Au electrode	Cyclic voltammetry Square wave voltammetry	-	0.13	[17]
Nano –Au/overoxidized polypyrrole composite/GCE	Cyclic voltammetry Differential pulse voltammetry	0.075 to 20	0.015	[18]
Tramella like grapheme Au composites/GCE	Cyclic voltmmetry Amperometry	0.8 to 2000	0.057	[19]
CTAB/Reduced graphene oxide-ZnS nanocomposite/GCE	Cyclic voltammetry	1 to 500	0.5	[20]
Nano Au-self assembled/GCE	Cyclic voltammetry Differential pulse voltammetry	0.01 to 25	0.004	[21]
Nafion carbon nanotubes coated poly(3-methylthiophene)/GCE	Cyclic voltammetry Differential pulse voltammetry	0.02- 0.1 0.10 -1.0 1.0- 6.0	0.005	11
Polyglycine/CuO nanoparticles	CV mode used Dp (Differential pulse)	0.3–1.4 2–20	0.055 0.18	10
AuNps distributed poly(4-aminothiophenol)/GCE	Cyclic voltammetry Differential pulse voltammetry	10-50	5.5	15
Nafion/Fr-AuNps	CV (Amperometry)	0.25-7	0.00183	This work

Conclusions

A facile, novel and rapid approach are reported here for the synthesis of AuNps employing Furosemide drug as reducing as well as capping agent. These Fr-AuNps were used to modify GCE in order to fabricate a sensor selective for DP. The modification of the sensing interface of GCE by Fr-AuNps offers higher sensitivity as well as selectivity towards oxidation of DP and successful detection of dopamine from human blood samples. The fabricated dopamine biosensor has a high potential for the determination of dopamine from biological and clinical samples. Thus, it is safe to say this is another alternative tool for the dopamine detection.

References

1. J Manjunatha, BK Swamy, G Mamatha, U Chandra, E Niranjana, et al. (2009) Cyclic voltammetric studies of dopamine at lamotrigine and TX-100 modified carbon paste electrode. Int J Electrochem Sci 4: 187-196.
2. P Calabresi, A Castrioto, M Di Filippo, B Picconi (2013) New experimental and clinical links between the hippocampus and the dopaminergic system in Parkinson's disease. The Lancet Neurology 12: 811-821.
3. JM Jarcho, EA Mayer, ZK Jiang, NA Feier, ED London (2012) Pain, affective symptoms, and cognitive deficits in patients with cerebral dopamine dysfunction. PAIN® 153: 744-754.
4. HX Zhao, H Mu, YH Bai, H Yu, YM Hu (2011) A rapid method for the determination of dopamine in porcine muscle by pre-column derivatization and HPLC with fluorescence detection. J Pharm Anal 1: 208-212.
5. L Zhang, S Qv, Z Wang, J Cheng (2003) Determination of dopamine in single rat pheochromocytoma cell by capillary electrophoresis with amperometric detection. J Chromatogr B 792: 381-385.
6. C Xue, Q Han, Y Wang, J Wu, T Wen, et al. (2013) Amperometric detection of dopamine in human serumby electrochemical sensor based on gold nanoparticles doped molecularly imprinted polymers. Biosens Bioelectron 49: 199-203.
7. X Ma, M Chao, Z Wang (2012) Electrochemical detection of dopamine in the presence of epinephrine, uric acid and ascorbic acid using a graphene-modified electrode. Analytical Methods 4: 1687-1692.
8. SS Kumar, J Mathiyarasu, KL Phani (2005) Exploration of synergism between a polymer matrix and gold nanoparticles for selective determination of dopamine. J Electroanal Chem 578: 95-103.
9. CL Sun, HH Lee, JM Yang, CC Wu (2011) The simultaneous electrochemical detection of ascorbic acid, dopamine, and uric acid using graphene/size-selected Pt nanocomposites. Biosens Bioelectron 26: 3450-3455.
10. S Reddy, BE Kumara Swamy, H Jayadevappa (2012) CuO nanoparticle sensor for the electrochemical determination of dopamine. Electrochim Acta 61: 78-86.
11. HS Wang, TH Li, WL Jia, HY Xu (2006) Highly selective and

sensitive determination of dopamine using a Nafion/carbon nanotubes coated poly(3-methylthiophene) modified electrode. Biosens Bioelectron 22: 664-669.
12. D Ravi Shankaran, N Uehara, T Kato (2003) Sol–gel derived metal dispersed ceramic–graphite composite electrode for amperometric determination of dopamine. Anal Chim Acta 478: 321-327.
13. NF Atta, A Galal, SM Azab (2012) Novel sensor based on carbon paste/Nafion(R) modified with gold nanoparticles for the determination of glutathione. Anal Bioanal Chem 404: 1661-1672.
14. YP Hsiao, WY Su, JR Cheng, SH Cheng (2011) Electrochemical determination of cysteine based on conducting polymers/gold nanoparticles hybrid nanocomposites. Electrochim Acta 56: 6887-6895.
15. AI Gopalan, KP Lee, KM Manesh, P Santhosh, JH Kim, et al. (2007) Electrochemical determination of dopamine and ascorbic acid at a novel gold nanoparticles distributed poly (4-aminothiophenol) modified electrode. Talanta 71: 1774-1781.
16. T Shaikh, A Nafady, FN Talpur, MH Agheem, MR Shah, et al. (2015) Tranexamic acid derived gold nanoparticles modified glassy carbon electrode as sensitive sensor for determination of nalbuphine. Sens Actuators B Chem 211: 359-369.
17. CR Raj, T Okajima, T Ohsaka (2003) Gold nanoparticle arrays for the voltammetric sensing of dopamine. J Electroanal Chem 543: 127-133.
18. J Li, X Lin (2007) Simultaneous determination of dopamine and serotonin on gold nanocluster/overoxidized-polypyrrole composite modified glassy carbon electrode. Sens Actuators B Chem 124: 486-493.
19. C Li, J Zhao, X Yan, Y Gu, W Liu, et al. (2015) Tremella-like graphene–Au composites used for amperometric determination of dopamine. The Analyst 140: 1913-1920.
20. YJ Yang (2015) One-pot synthesis of reduced graphene oxide/zinc sulfide nanocomposite at room temperature for simultaneous determination of ascorbic acid, dopamine and uric acid. Sens Actuators B Chem 221: 750-759.
21. GZ Hu, DP Zhang, WL Wu, ZS Yang (2008) Selective determination of dopamine in the presence of high concentration of ascorbic acid using nano-Au self-assembly glassy carbon electrode. Colloids Surf B Biointer 62: 199-205.