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Cobalt Ferrite Nanoparticles Modified Glassy Carbon Electrode for the Voltammetric Detection of Dopamine

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Abstract- Cobalt ferrite nanoparticles (CFNs) were successfully synthesized by a wet chemical method. The morphology and that of the crystal structure of the synthesized nano ferrites was done by X-ray diffraction analysis and Transmission electron microscopy techniques. The crystalline size of the synthesized nanoparticles was in the range of 30 nm calculated by the Debye-Scherrer equation. A glassy carbon electrode (GCE) modified with the ferrite nanoparticles (CFNs) was employed for the electrochemical detection of dopamine using the techniques of cyclic voltammetry and differential pulse voltametry. The chemically modified electrode exhibited exceptional redox action for the detection of dopamine (DA), with a notable decline of overpotential while compared to bare GCE. The CFNs/GCE exhibited excellent stability, reproducibility and sensitivity in the determination of DA with a detection limit of 0.2 μm. The sensor exhibited appreciable electrocatalytic behavior in the simultaneous detection of ascorbic acid (AA), Dopamine (DA) and Uric acid (UA).

Keywords- Ascorbic acid; Uric acid; Differential pulse; Electrochemical; Simultaneous

1. INTRODUCTION

Dopamine (DA) is one of the most essential neurotransmitters which plays a significant role in the cardiovascular, renal and central nervous system [1,2]. It is also a naturally occurring

biogenic compound notable for its inhibitory neurotransmitter [3]. As a therapeutic drug DA is used to reduce the risk of renal failure by increasing the renal blood flow [4,5]. Dopamine hydrochloride is widely accepted in the treatment of bronchial asthma, hypertension, heart failure, cardiac surgery and renal failures [6]. However, overusage of DA has been coupled with adverse effects on the central nervous system, drug addiction even in Parkinson's disease. Hence the detection of the present compound gains prime importance [7-9]. Different methods have been reported for the detection of DA including spectrophotometry [10-12], HPLC method [13], chromatography [14] and fluorescence [15]. However, these methods suffer some of the common problems like long time analysis, high costs, poor selectivity and low sensitivity. As, DA is an electro active molecule, electrochemical methods find significant application, which can offer the opportunity for portable, cheap and rapid methodologies with excellent sensitivity [16]. Electrochemical methods by using chemically modified electrodes have been the area of research now-a-days. A wide variety of modifications including polyprrrole derivatives, graphene, carbon nanotubes, metal complexes have been reported for the detection of DA [17-20]. Amongst these, nanoparticles modified electrodes deserve special attraction on behalf of their significant electrocatalytic properties and enhanced surface area. However, no report is available concerning the use of cobalt ferrite magnetic nanoparticles as electrode modifying material for the detection of DA.

Magnetic Cobalt ferrite nanoparticles have become one of the most fascinating and catalytically enriched materials among the family of spinels. The attractive crystalline framework and exceptional properties highlights the superiority of the same. CFNs were known for its high cubic magneto crystalline anisotropy, chemical stability, mechanical hardness accompanied by a reasonable saturation magnetization [21]. Moreover, the excellent surface area exhibited by them makes them better candidates in sensing purposes.

Herein we present a cobalt ferrite nanoparticle modified electrode for the detection of DA. The particles were synthesized by a wet chemical method. The present method has the specific benefit of shape-effectiveness and the extent for conveyance focusing the apparent perfection of the crystal. The smoothness of alteration of the electrode by plummeting and aeration is one of the uniqueness of the present approach and is totally green exclusive of any detrimental chemicals.

2. EXPERIMENTAL

2.1. Chemicals

Ferric nitrate [$Fe(NO_3)_3.9H_2O$], Cobalt nitrate [$Co(NO_3)_2.6H_2O$], and citric acid ($C_6H_8O_7$) were obtained from Merck. The solutions of the corresponding nitrates (0.1 M cobalt and 0.2 M iron) were obtained by dissolving the stoichiometric amount in double distilled water. Acetaminophen, dopamine and ascorbic acid were purchased from Aldrich (USA). The buffer

solution was prepared by using 0.1 M KH_2PO_4 (Merck) and the desired pH was adjusted by using 0.1 M KOH or 1:1 H_3PO_4. The chemicals employed were of analytical-reagent grade.

2.2. Instrumentation

Electrochemical experiments were performed using an Electrochemical analyzer CHI 604D (CH Instrumental Co. USA). A bare glassy carbon electrode [GCE], 3 mm and cobalt ferrite nanoparticles modified glassy carbon electrode [CF/GCE] acts as the working and Ag/AgCl, KCl (saturated) as the reference electrode respectively. Cyclic voltammetric experiments (CV) were carried out in a quiescent solution at 100mVs^{-1} in an electrochemical cell having 10ml of buffer solution (supporting electrolyte). The measurements were performed at room temperature (23±5 ℃). Further, oxygen was not removed from the measured solutions. X-ray diffraction (XRD) studies were recorded on a Bruker AXS D8 ADVANCE X-ray diffractometer with Cu/Kα radiation (1.5406 Å). Morphology was observed by means of Transmission electron microscopic (TEM) with PHILIPS CM200 having an operation voltage of 20-200 Kv. A digital pH-meter was used for measuring the pH.

Cyclic voltammetry was employed for the first part of the studies. The difference in the electrochemical behavior of the modified as well as bare electrodes were done using voltammograms recorded in the potential range from -200 mV to 800 mV with a scan rate of 50 mVs^{-1}. Similar potential range was selected for the scan rate studies where; the scan rate was varied from 20 mVs^{-1} to 250 mVs^{-1}. Linear sweep voltammetry was used to study the effect of pH on the system and the potential range was from -200 mV to 800 mV at a scan rate of 50 mVs^{-1}. Differential pulse voltammetry was utilized for studying the effect of concentration on the present analysis. DPV was used having optimized parameters in the potential range from -200 mV to 600 mV with a pulse height of 50 mV, pulse width 10 ms and a scan rate of 50 mVs^{-1}.

Before every measurement, the CF/GCE surface was rinsed with deionized water followed by anodic and cathodic pretreatments. The electrode was anodically pretreated by applying a potential of +2 V for 60 s in 1 mol L^{-1} HNO_3 solution. The cathodic pretreatment was carried out at -2 V during 60 s in order to attain hydrogen termination of electrode surface. Further rinsed with deionized water and is polished using silk cloth until a mirror like finish appeared. And finally, to attain a stable response 50 cyclic voltammograms ranging from -0.2 V to 800 mV in the solution of 0.1 M PBS was carried out.

Origin Pro 8.5 (Origin Lab Corporation, Northampton) was employed for the studies of calculating linear least square regression and for the evaluation of calibration curve. The detection limit was calculated as three times the standard deviation for the blank solution (supporting electrolyte) divided by the slope of the calibration curve.

2.3. Synthesis of Cobalt ferrite nanoparticles

Cobalt ferrite nanoparticles were prepared using a wet chemical method according to our previous publication [21]. Only an observable change is the variation of the calcination temperature at 700 ℃ for 3 hours.

2.4. Preparation of the CFNs/GCE

Cobalt ferrite nanoparticles (2 mg) were dispersed in 1mL N,N dimethyl formamide and agitated in an ultrasonic bath for an hour to achieve a well dispersed suspension. Prior to use, the GCE was polished with 0.05 μm α-Al_2O_3, rinsed ultrasonically with water, absolute ethanol and double distilled water respectively. In order to modify, 5 μL of CFNs suspension be cast on the surface of the pre-treated GCE and left to dry at room temperature. The modified electrodes were represented as CFNs/GCE.

3. RESULTS AND DISCUSSION

3.1. Characterization of Cobalt ferrite nanoparticles

Figure 1 shows the XRD patterns of $CoFe_2O_4$ calcined at 700 ℃. The corresponding (2 2 0), (3 1 1), (2 2 2), (4 0 0), (5 1 1) and (4 4 0) is in agreement with JCPDS file 22-1086, indicative of cubic spinel structure (Fd3m) [22]. The particle size was determined from the full width at half maximum (FWHM) using Scherrer formula and was found to be 30 nm. The transmission electron micrograph of the cobalt ferrite nanoparticles illustrates (Figure 2) that they have uniform spherical morphology, weakly agglomerated, also fine size distribution. The particle size 30 nm matches well with the X-ray powder diffraction peaks. Moreover, the sample exhibited a saturation magnetization of 20 emu/g and coercivity 822 G.

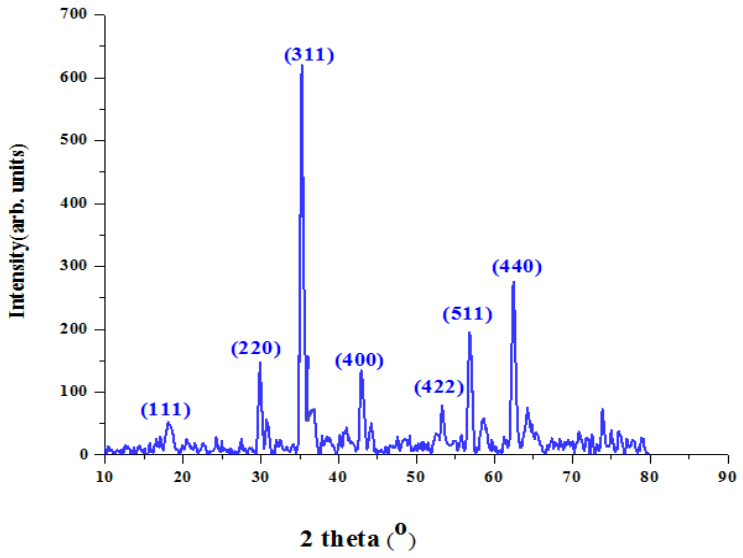


Figure 1. XRD patterns of cobalt ferrite nanoparticles

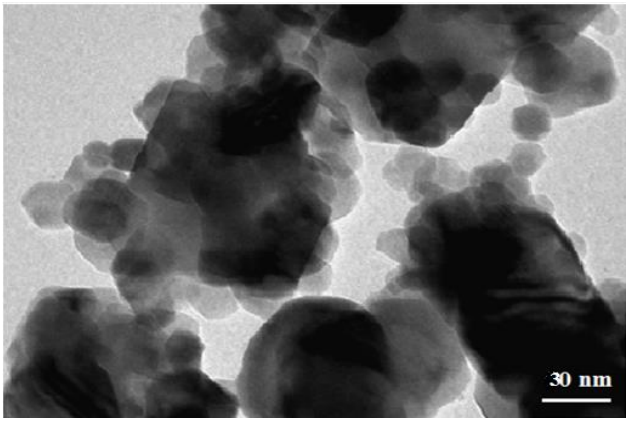


Figure 2. TEM image of Cobalt ferrite nanoparticles

3.2. Electrochemical behavior of DA

Figure 3 shows typical cyclic voltammograms of bare glassy carbon and CFNs/GCE in 0.1 M PBS solution (pH 6) containing 20 mM of DA. The peak potential separation between the E_{pa} and E_{pc} (56 mV) is found to be smaller in the case of the modified electrode. Moreover, the current obtained was twice the values that obtained for bare GCE. The significant peak current and reduced peak separation are strong evidences for the catalytic property of the modified electrodes. Furthermore, the oxidation peaks also shifted from 0.228 V to 0.106 V for the modified electrode. These results are indicative of the outstanding electrochemical response of the modified electrode towards the detection of DA. This may be attributed to the larger effective surface area of CFNs and the static interaction between the negatively charged species and electropositive DA molecules. The redox reaction that involved in the DA mechanism can be explained as the oxidation of DA to dopaminequinone and the reduction of the latter to DA and the probable mechanism can be described as follows (Scheme 1) [23].

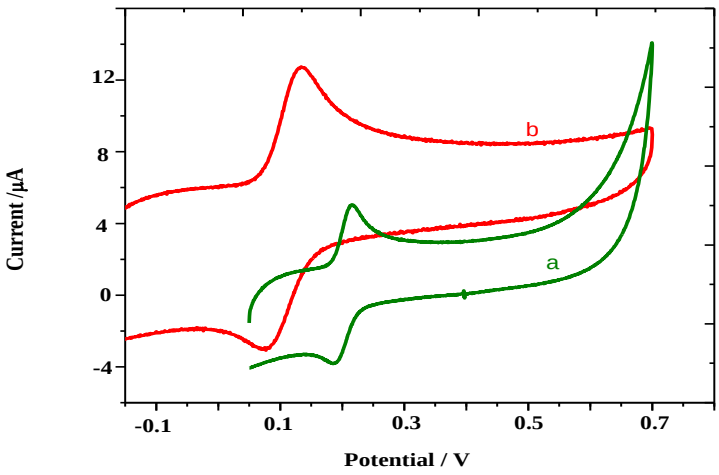
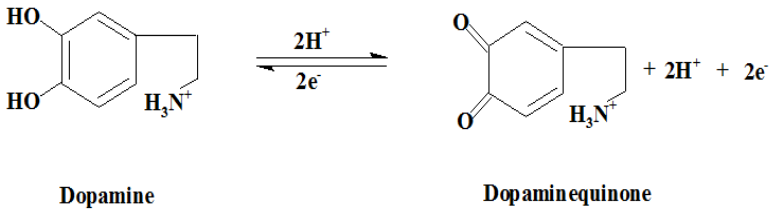


Figure 3. CVs at bare GCE (a) and CFNs/GCE (b) in 0.1 M PBS (pH 6.0) containing 20 mM DA. Scan rate: 0.5 V/s



Scheme 1. Mechanism of the oxidation reaction of dopamine

3.3. Effect of Scan Rate

The effect of scan rate on the electrochemical behavior of DA was studied by using cyclic voltammetry at the modified electrode. The scan rate was varied from 20 mV to 200 mV in 0.1 M PBS solution containing 20 mM DA. It was found from Figure 4 that both the anodic and cathodic peak currents increased with an increase in scan rate. The peak currents were observed to follow a linear relationship (Figure 4B) with the square root of scan rate indicative of a diffusion-controlled process [24-26].

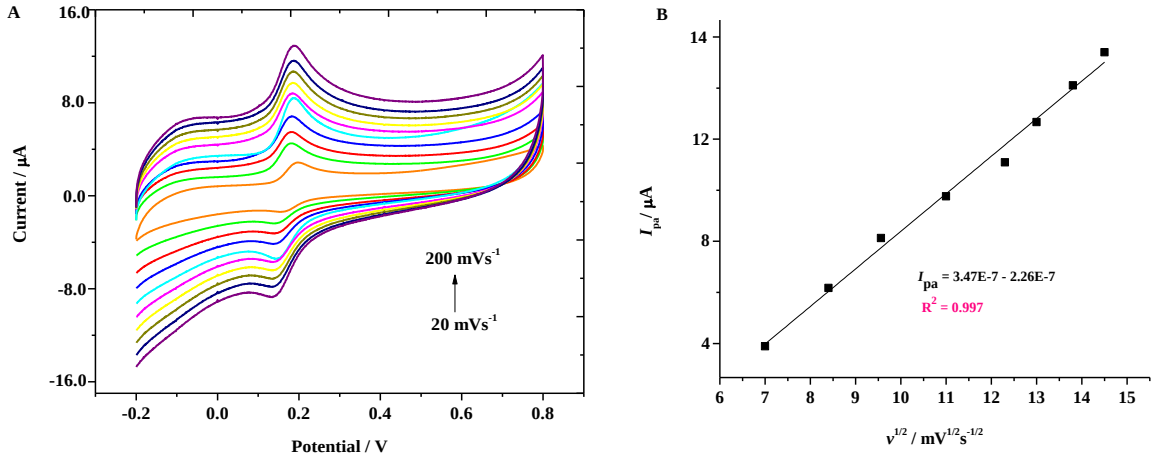


Figure 4. (A).CVs acquired on CFNs/GCE with 20 mM DA in 0.1 M PBS (pH 6) at different scan rates from 20 to 200 mVs^{-1}. (B) . Linear relationship of DAVs scan rate.

3.4. Effect of pH

The pH plays a significant role in controlling the electrochemical behavior of DA by varying the peak potentials and peak currents. From the Figure 5A, it was observed that as the pH value increased from 3.0 to 8.0 the peak potentials of DA shifted to more negative values, indicating that protons took part in the electrode reaction. The oxidation peak potentials for DA on the CFNs/GCE vary linearly with pH as shown in Figure 5B. The corresponding slope of -57 mV is very close to the theoretical value of -59 mV, suggesting that the redox process of

DA involves two protons and two electrons which are in agreement with the previous reports [27-30]. Furthermore, the peak current was found to be maximum at a pH of 6.0 and is used for further investigations.

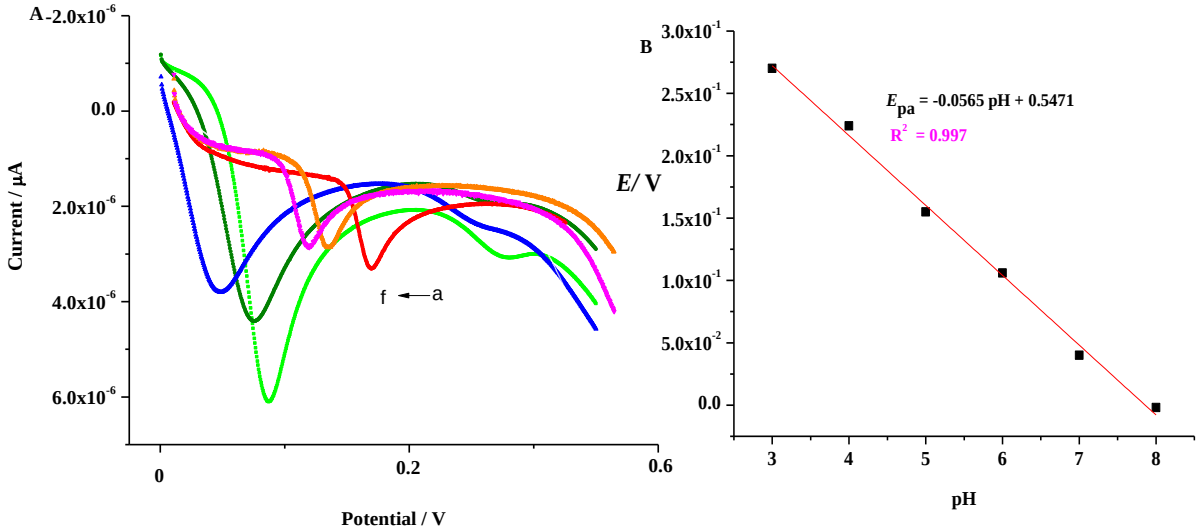


Figure 5. (A) LSVs of 20 mM DA on 0.1 M PBS at different pH values (a-f): 3.0, 4.0, 5.0, 6.0, 7.0 and 8.0. (B) Linear relationship of E_{pa} *vs.* pH

3.5. Effect of concentration

Under selected conditions, the modified electrode was employed to study the determination of different concentrations of DA. Figure 6A shows the differential pulse voltammetry of the modified electrode towards the detection of DA at different concentrations at a pH of 6.0.

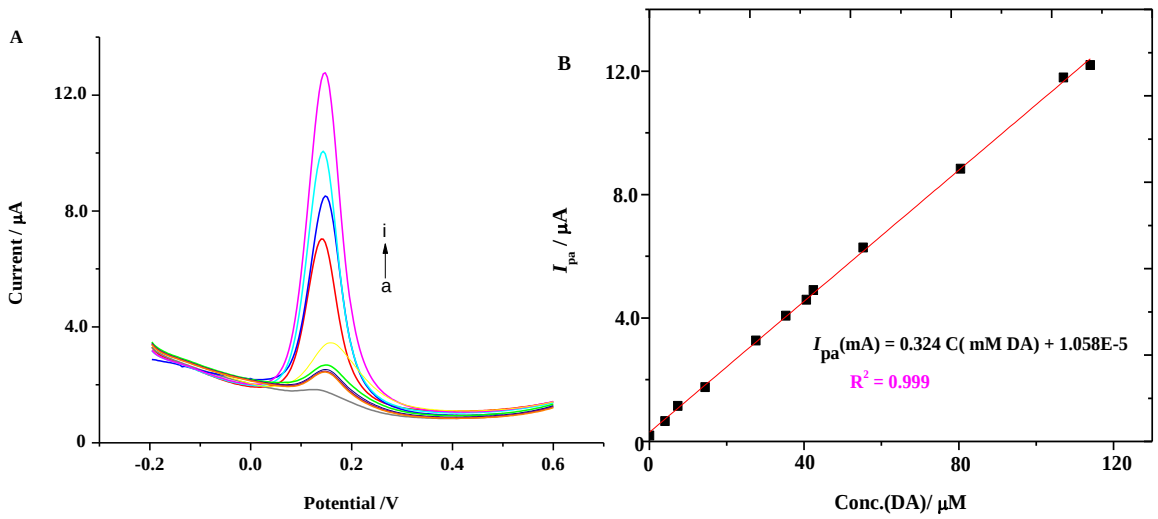


Figure 6. (A) DPVs of DA at CFNs/GCE at different DA concentrations (pH = 6.0) (a-o; µM) a) 0.09 b) 0.4 c) 7.3 d) 15 e) 25 f) 40 g) 42 h) 55 i) 100 (B). Linear relationship of current Vs concentration of dopamine

An outstanding increase in peak current was noted with an increase in concentration suggesting that the present electrode could be applied for the detection of DA. The anodic peak current increased linearly from a range of 0.09 μM to 100 μM with a detection limit of 0.2 μM (S/N = 3) which was lower than some of the available reports [31-36], also with respect to other chemically modified electrodes (Table 1).

Table 1. Comparison of analytical parameters towards the detection of DA

Sl. No.	Electrode Surface	Detection Range	LOD	Reference
1	Polyaniline (PANI)/Metal oxide NiO, ZnO, Fe_3O_4	2-20 μM	3.3 μM	[37]
2	GO/Fe_3O_4	1-10 μM	0.48 μM	[38]
3	α-Fe_2O_3/rGO/GCE	1.0×10^{-8}-9.0×10^{-4} M	3.26 nM	[39]
4	3D-rGO/β-CD	0.5-100 μM	0.013 μM	[40]
5	N-rGO/Fe_3O_4 NRs/GCE	0.2-176 μM	0.05 μM	[41]
6	CFNs/GCE	0.09-100 μM	0.2 μM	Present work

The reproducibility was examined by repetitive measurement of oxidative peak current of 10 μM DA in 0.1 M PBS. After each determination, the used modified surface was regenerated by repetitive cycling at a scan rate of 50 mV s^{-1} for 2 hours. After several successive measurements, only slight deviation (RSD = 0.45 %) was noted indicative of the substantial stability exhibited by the modified electrode.

3.6. Simultaneous detection of DA, AA and UA at CFN/GCE

DA, AA and UA are the important biomolecules which co-exist in the central nervous system and plays a significant role in human metabolism [42]. Thus, the simultaneous detection of DA in presence of the compounds like AA and UA has been studied by using DPV in 0.1 M PBS. As shown in Figure 7, a single broad overlapped peak was obtained for bare GCE when placed in a mixture containing millimolar levels of AA and micromolar levels of UA and DA. However, three well defined peaks were obtained at the modified electrode, CFNs/GCE with appreciable potential separations of 98 mV, 305 mV and 403 mV between AA-DA, DA-UA and UA-DA respectively. The enhancement in peak current and the improved separations of peak potentials are clear indicative of the modified electrode to be applicable for the selective and simultaneous detection of the three compounds.

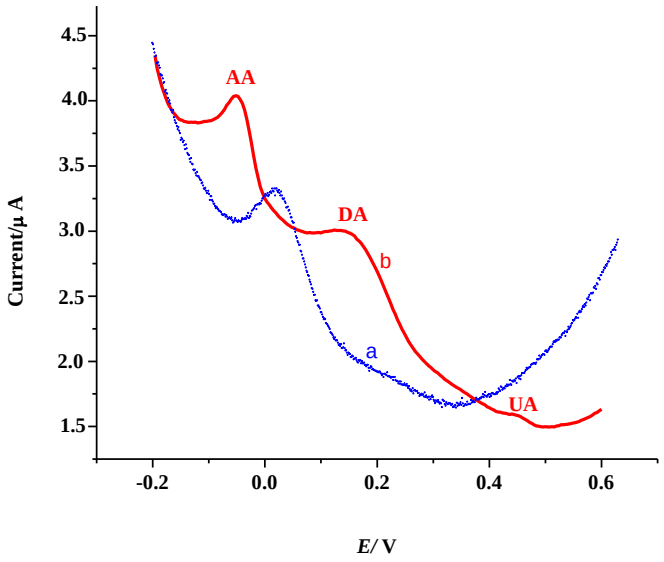


Figure 7. DPVs recorded at a) bare GCE b) and the CF/GCE with ACOP (10 μM), AA (10 mM), DA (10 μM) in 0.1 M PBS (pH 6)

3.7. Determination of DA in Real Sample Analysis

The modified electrode was utilized for the real sample analysis. Dopamine Hydrochloride Injection purchased from the analytical lab was used for the purpose. The DA sample was diluted using 0.1 M PBS. Table 2 presents the accuracy of the method. The obtained results were indicative of the applicability of the modified electrode in the field of pharmaceutical analysis.

Table 2. DA detection in Dopamine Injection Sample

Sample	Content (mg/ml)	Detected (mg/ml)	RSD (%)	Recovery (%)
1	40	39.98	1.8	98.2
2	40	41.23	1.7	101.3
3	40	41.92	1.8	100.8

4. CONCLUSION

In the present work, cobalt ferrite nanoparticles having an average particle size of 30 nm have been successfully synthesized by a wet chemical route. The material was used to modify the electrode surface using the simplest way of drop-dry. The studied electrode reaction followed a diffusion-controlled process. The linear dynamic range for DA detection was from 0.09 μM to 100 μM showing a detection limit of 0.2 μm. Finally, the present analytical method has successfully applied for the selective and simultaneous detection of AA, DA and UA with excellent potential separation. The outstanding electrocatalytic property combined with the

electrochemical technique can be considered as a sensitive and environmentally acceptable tool for the analysis of DA.

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