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RESEARCH ARTICLE

Simultaneous Determination of Dopamine in Presence of Ascorbic Acid with Fe-Ag CTAB Nanoparticles Carbon Paste Electrode

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Abstract: A novel electro-chemical method was designed to develop a simple, inexpensive, selective and sensitive electrochemical sensor by modifying carbon paste electrode for the simultaneous determination of dopamine (DA) without the interference of ascorbic acid (AA). Chemically modified carbon paste electrode was prepared by the incorporation of iron-silver bimetallic nanoparticles (Fe-AgNps/Fe-AgCTABMCPE) in presence of cationic surfactant Cetyltrimethyl ammonium Bromide (CTAB) was used for the surface modification and the properties of the modified electrode was studied by using the analytical techniques like cyclic voltammetry (CV), differential pulse voltammetry (DPV) and scanning electron microscope (SEM) image. The modified electrode showed a couple of distinct and well-defined redox peaks for DA and AA mixture, which was not observed with bare carbon paste electrode in 0.1 M phosphate buffer solution (PBS) of pH 7.0 with a scan rate of 50 mVs^{-1}. There was a good enhancement in redox peak current for DA by 3 folds when compared to bare carbon paste electrode. The anodic peak current *vs.* scan rate was found to be linear with a correlation coefficient of 0.9951 indicating that the reaction is a diffusion controlled process. The anodic peak current (Ip_a) showed a linear relation with concentration of DA with a correlation coefficient of 0.9986 and the detection limit was found to be 3.52×10^{-5} M. The detection limit of DA is 0.01 μM with a correlation coefficient of 0.9953 and AA is 0.4 μM with a correlation coefficient of 0.9952 respectively. Hence this chemically modified electrochemical sensor showed a reliable result for the voltammetric determination of AA in the presence of DA and it can be ideal for the practical application of DA in human blood serum and dopamine hydro chloride injection.

Keywords: Fe-Ag bimetallic nanoparticles, Cetyltrimethyl ammonium bromide surfactant, Dopamine, Ascorbic acid, Scanning electron microscopy, Voltammetric techniques

Introduction

Selectivity is the inherent property of biologically important molecules which facilitate the introduction of novel electro analytical device. The electrical signal provides simultaneous sensitive detection technique for Dopamine (DA) and Ascorbic acid (AA) which are usually

coexisting as body fluids and play a vital role in human metabolism. Dopamine (DA) is a simple organic molecule which was discovered in the year 1950. It is an important inhibitory monoamine neurotransmitter compound from the dopaminergic neurons of the midbrain[1]. DA consists of aromatic diol group which is derived from the amino acid tyrosine[2]. DA is (3, 4-dihydroxyphenethylamine) an important chemical messenger which is responsible for controlling emotions, responses and other body movements[3,4]. Normally, DA level in human blood plasma exists in the range of 0.04 to 4.50 nM[5], high concentration levels of DA 50 n mol/g in the brain region is known as "caudate nucleus"[6] and low concentration levels of DA in the "extracellular fluid" ranges from 0.01 to 1×10^{-6} mol L^{-1}. It plays a vital role in functioning of central nervous, cardiovascular, hormonal and renal systems[7]. It has a positive chronotropic and ionotropic effects on myocardium which stimulates cardiac contractility and enhances heart beat rate. Renal failure, blood pressure and increased heart beat show high levels of dopamine in mesolimbic pathway and low levels of dopamine in the prefrontal cortex[8, 9]. Different concentration levels of DA in the body leads to various neurodegenerative diseases such as Huntington's, burning mouth syndrome[10] Schizophrenia, restless leg syndrome[11], epilepsy, Senile dementia, fibromyalgia[12,13] Alzheimer's and HIV[14-17]. Depletion of DA in cerebral region is the hall mark for Parkinson's disease[18].

L-Ascorbic acid (or) vitamin-C is a water soluble vitamin which plays a potential role in the physiology of neuronal properties such as antioxidant, pH regulator[19], enzyme co-factor and neuromodulator in the brain[20]. It has been used in the treatment of mental illness, common cold, cancer and AIDS[21]. It is a vital compound in human diet. Thus, the determination of these two biomolecules is important not only in the field of biomedical chemistry and neurochemistry but also for diagnostic and pathological research[22,23].

Earlier analytical methods like fluorimetry[24], chemiluminescence(CE-luminescence)[25], capillaryelectrophoresis[26], chromatography[27], ultraviolet–visible spectrophotometry[28], *etc.*, are high cost, time consuming and it require complex pretreatment. However, it is essential to develop a simple, inexpensive, fast analysis, with high selectivity and sensitivity[29] methods for the preparation of different nano carbon modified electrodes like $LaFeO_3$ nanoparticles modified electrode[30], gold nanoparticles-*β*-cyclodextrin–grapheneGCE[31,33], reduced Graphene Oxide-Palladium-Nano Particles composite electrode[34], pyrolitic graphite modified electrode[35], Pt–Au hybrid film modified electrode[36], palladium nanoparticle-loaded carbon nanofibers modified electrode[37], cetyl pyridine bromide/chitosan composite film-modified glassy carbon electrode[38], mesoporous carbon materials[39], electro spun carbon nanofibers[40] and other nano metal oxides of MCPE[41,44].

Recently, many researchers have focused on synthesizing different nano particles as their size, shape, electrical, chemical, magnetic and mechanical properties[45] have attracted the great attention in both fundamental science and applied research. Sinfelt *et al*. have made series of studies on different bimetallic nanoparticles, with well defined nobel metals and alloy structures like Cu-Pd[46], Pt-W[47] Ag-Pt[48], Ag-Co[49], Ag-Ni[50], Au-Pt[51], Pt-Ru[52] *etc*., particularly Fe-Ag nano particles have attracted the great interest because of their structural, electrical, optical, catalytical and thermal properties[53,57]. Fe-Ag alloy is such a two-component alloy system consisting of magnetic iron and nonmagnetic silver metal. The Fe-Ag nano particles were synthesized by chemical method with high concentration of Ag and low concentration of Fe because Ag has more electro activity and good stability.

Hu's group[58,60] was first studied the use of surfactants in electroanalytical chemistry to improve the detection limits of some biomolecules. Surfactant is a linear molecule with a unique molecular structure like hydrophilic head on one side and long hydrophobic tail on other side. Surfactants were extensively used in electro analytical chemistry because of their two properties (a) adsorption at interfaces and (b) aggregation into supramolecular structures[61] Chengguo Hu and Shengshui Hu[62] studied that CTAB form a compact monolayer on the electrode surface with high density of positive charge.

In this work, we aimed to develop a novel electro chemical sensor with bare carbon paste electrode deposited with Fe-Ag nano particles and surface modification with surfactant CTAB. This resulted in a technique with high stability, good electro catalytic activity and excellent conductivity. So, the modified electrode acts as a good voltammetric sensor for the simultaneous determination of AA and DA in clinical and pharmaceutical analysis.

Experimental

Analytical grade dopamine (DA), ascorbic acid (AA), sodium hydrogen orthophosphate (NaH_2PO_4), disodium hydrogen phosphate (Na_2HPO_4), perchloric acid, silicon oil were procured from Himedia chemicals. Fine graphite powder (particle size <20 μm) was supplied from Sigma-Aldrich. Dopamine stock solution (25 mM) was prepared by dissolving in perchloric acid, Phosphate buffer (pH 7.0) was prepared with 0.2 M NaH_2PO_4 and Na_2HPO_4 solution in distilled water. Chemicals were used as supplied without any further purification.

Instrumentation

All voltammetric experiments were performed with a CH-Instrument Model no.CHI 610D, Electrochemical work station connected to a personal computer was used for electrochemical measurements and data storage. A conventional three electrode cell was employed throughout the experiments, with bare and Fe-Ag modified carbon paste electrode (homemade cavity of 3.0 mm diameter) as a working electrode, Ag/AgCl electrode as a reference electrode and platinum wire as a counter electrode.

Preparation of bare carbon paste electrode

The carbon paste electrode was prepared by hand mixing of graphite powder and of silicon oil in the ratio of 70:30(w/w) in an agate mortar until homogeneous carbon paste was obtained. Then the prepared carbon paste was incorporated into 3.0 mm diameter of Teflon cavity current collector and polished using the soft paper before application.

Synthesis of bimetallic nanoparticles (Fe-Ag)

Fe-Ag bimetallic nanoparticles were synthesized by taking mixtures of ferric nitrate ($Fe(NO_3)_2 \cdot 9H_2O$) and silver nitrate ($AgNO_3$) by using chemical method and poly vinyl pyrrolidone (PVP) as a stabilizing agent. $Fe(NO_3)_2 \cdot 9H_2O$ (0.06 M) and $AgNO_3$ (0.04 M) was added into two-neck round bottom flask containing deionized water acting as a solvent and this reaction mixture was placed in a sonicator bath. The reaction mixture was carried out at room temperature for about 30 minutes to facilitate uniform mixing of the precursors and flushing out oxygen from the flask. After 10 minutes, a reducing agent *i.e.* the alkyl solution of sodium borohydride was added drop wise into the reaction mixture. After the addition of the reducing agent, sonication was continued for about another one hour and ninety minutes. There after the reaction mixture was allowed to cool at the room temperature for about two hours and the reaction mixture was dropped into a flask containing 100 mL of ethanol. The nanoparticles which were settled at the bottom of the flask were separated by centrifuging and repeatedly washed in ethanol[63].

Fabrication of Bi-metallic Modified carbon paste electrode

Carbon paste electrode (CPE) was modified by taking different weights of Fe-Ag bimetallic nano particles (2,4,6,8 and 10 mg) in the ratio of (70:30) graphite powder and silicon oil. This mixture was thoroughly mixed in an agate mortar for about 40 min to get a homogenous paste and it was packed into 3.0 mm diameter of Teflon cavity current collector and polished on a piece of soft paper before measurement.

Results and Discussions

SEM analysis

Figure 1 shows the SEM image for the synthesized Fe-Ag bimetallic nano particles. These SEM image shows that the Fe-Ag nanoparticles are uniformly dispersed on the electrode surface with a range of 5 nm. Finally the SEM analysis shows that the Fe-Ag nanoparticles are uniformly distributed on the electrode surface.

Electrochemical response of DA at the Fe-Ag nanoparticles modified CPE (Fe-Ag MCPE)

Figure 2 shows the concentration effect of Fe-Ag bimetallic nanoparticles in the presence of 1 mM DA with a supporting electrolyte of 0.1 M PBS at (pH 7.0). The modified carbon paste electrode with Fe-Ag MCPE showed a good enhancement in the anodic and cathodic peak current at 6 mg when compared with bare carbon paste electrode. It is due to substantial increase in peak current and decrement in the peak potential with a reversible electron transfer process and it suggests that the DA is efficiently oxidized at Fe-Ag nano modified carbon paste electrode (Fe-Ag NMCPE).

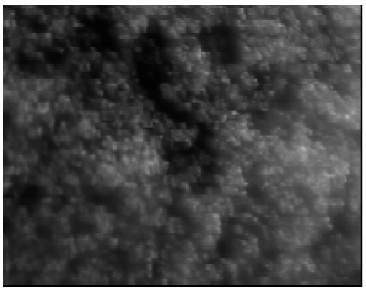

Figure 1(a). SEM image of Fe-Ag nanoparticle

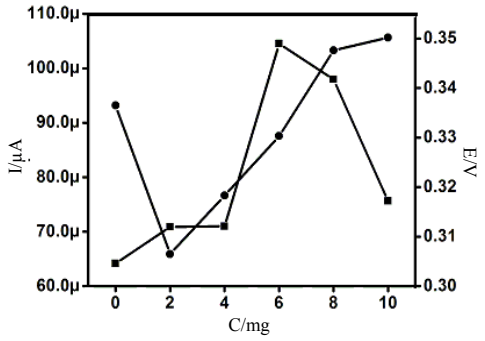

Figure 2. Concentration effect of Fe-Ag bimetallic nanoparticle on anodic peak current (Ipa) and anodic peak potential (Epa) in 0.1 mM DA and 0.1 M phosphate buffer solution at scan rate 50 mVs^{-1}.

Electro catalytic oxidation of DA at bare CPE and Fe-Ag MCPE

Figure 3 shows the cyclic voltammogram response for the electrochemical oxidation of 1 mM DA with a supporting electrolyte of 0.1 M phosphate buffer solution (pH 7.0) at a scan rate of 50 mVs^{-1}. At bare CPE (dashed line) DA showed a pair of poor redox peaks with high anodic peak potential (Epa) 0.251V and cathodic peak potential (Epc) 0.137 V respectively with a low current response. Under the same conditions Fe-Ag nano MCPE (solid line) showed a decrement in anodic peak potential (Epa) of 0.217V and cathodic peak potential (Epc) 0.148 V with a good reversible electron transfer process and the peak current

was enhanced by 3 folds when compared to the bare CPE, with a well defined redox peak for DA was observed. An intensive increase in the peak current was observed owing to the improvement in reversibility for an electron transfer process.

Effect of scan rate on dopamine

Figure 4 explains the effect of scan rate on redox peaks of DA (1mM) with a supporting electrolyte of 0.1 M PBS at pH 7.0. By increasing the scan rate, both the anodic peak current and the cathodic peak current were linearly proportional to the scan rate (υ) in the range of 50 to 400 mVs^{-1} to study the kinetics of an electrode reaction. The anodic peak potentials were shifted gradually towards the positive direction and the cathodic peak potentials were shift towards the negative direction with a correlation coefficient (R^2) of 0.9975. The above results indicate that the electrode reaction of DA is controlled by diffusion process.

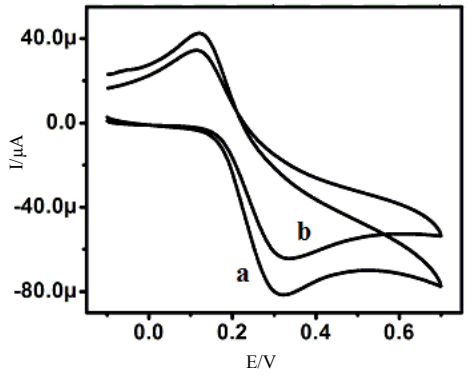

Figure 3. Cyclic voltammograms for the electrochemical response of 0.1mM DA (a) bare carbon paste electrode (dotted line) (b) Fe-Ag modified carbon paste electrode (thick line) in 0.1 M phosphate buffer solution at pH 7.0 3.4

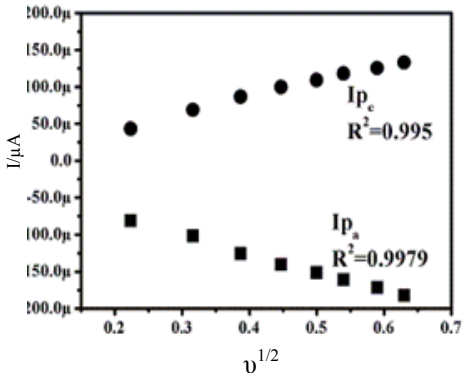

Figure 4. Cyclic voltammograms shows linear relationship between the peak current and scan rate

Influence of pH

In most cases, the pH of a solution is considered as an important factor that affects an electrochemical reaction. Different experiments were carried out in various supporting buffers like acetate and phosphate with different pH values in order to assess their impact on the monitored electro analytical signal. The results were obtained with Fe-Ag nano MCPE, its sensitivity was accompanied with sharper response in 0.1 M phosphate buffer solution. Therefore, the supporting electrolyte pH was varied from 5.5 to 8.0 and carried out the experiment with target concentration of 1 mM DA with a scan rate of 50 mVs^{-1}. Maximum anodic peak current was observed at pH 7.0 revealing that the proton takes part in the electrode reaction of DA. Thus, the pH 7.0 was selected for all the subsequent electrochemical analysis of DA as shown in Figure 5. The effect of pH on the peak currents and peak potentials demonstrates that it is an electron and proton transfer process[41].

Concentration effect of dopamine at Fe-Ag nanoMCPE

The electro catalytic oxidation of DA was carried out using differential pulse voltammetric technique using Fe-Ag nano MCPE for different concentrations of DA in 0.1 M phosphate

buffer solution (PBS). From Figure 6 it is clear that the anodic peak current was increased linearly with DA concentration. A good linear relationship ranges from 0.01 μM to 0.4 mM with three different linear ranges ranging from 0.01 μM to 0.3 μM, 0.4 μM to 0.1 mM and 0.2 mM to 0.4 mM. The correlation coefficients for these three linear graphs were 0.99447, 0.99861 and 0.99335 respectively as shown in Figure 6. The analytical method was validated with respect to parameters such as limit of detection (LOD) and limit of quantification (LOQ). The detection limit for DA in the lower range region was found to be 0.05 μM and quantification limit was 1.187×10^{-7} M for Fe-Ag MCPE, these limits were calculated according to the formulae of LOD $=3S_b/S$ and LOQ $=10S_b/S$ where S_b is standard deviation of intercept and S is slope of the calibration graph.

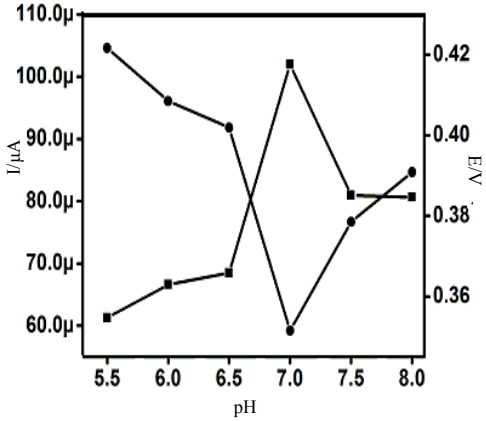

Figure 5. Effect of pH on oxidation of anodic peak current (Ipa) and anodic peak potential (Epa) of DA in 0.1M PBS (5.5-8.0)

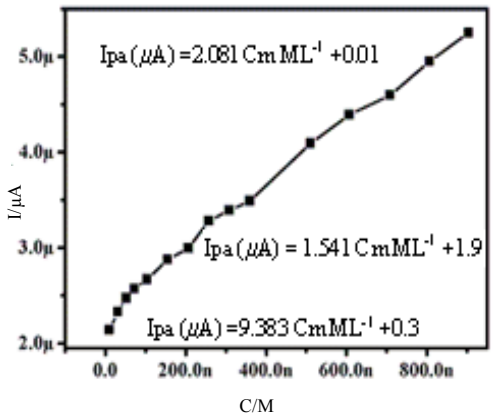

Figure 6. DPVs for various concentration of DA in the presence of 0.1 M phosphate buffer

Electrochemical response of dopamine in presence of ascorbic acid at Fe-Ag modified carbon paste electrode with CTAB

DA and AA are biologically important compounds which coexist in serum and the extracellular fluid of the central nervous system. We aimed to determine the ability of modified electrode for the selective species. Cyclic voltammogram was recorded with a physiological 0.1 M phosphate buffer solution (pH 7.0) at a scan rate of 50 mVs^{-1}. The electrochemical response obtained for DA and AA is shown in Figure 7 and the peaks were not resolved with bare CPE and Fe-Ag nano MCPE in absence of cationic surfactant CTAB (dotted line-a & thick line b). It is due to complex properties, irreversible reaction and requirement of high over potential and fouling of the electrode by the adsorption of oxidized product (AA). However, Fe-Ag nano MCPE with cationic surfactant CTAB showed a good enhancement in presence of 50μL of $3x10^{-5}$M CTAB, reflected by the enlargement of anodic peak current (*Ipa*) (thick line-C) of each analyte with a peak potential of 0.075 V, because the cationic surfactant CTAB molecule diffuses into the carbon paste electrode along with AA and DA. Therefore, Fe-Ag CTAB nano MCPE prevents the fouling of the electrode surface, irreversible reaction and faster electron transfer and kinetics of DA. Since the oxidation peak of DA is shifted to less positive potential, it has not interfered with the measurement of AA.

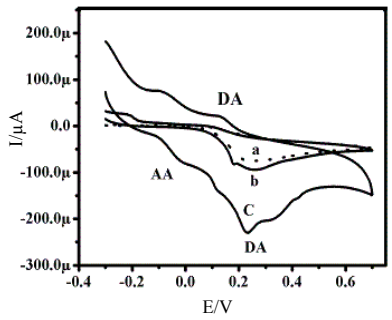

Figure 7. Electrochemical response of 0.1 mM Dopamine, 1 mL ascorbic acid on the bare carbon paste electrode (dotted line-a), Fe-Ag MCPE (thick line-b) and the Surface Fe-Ag CTAB MCPE (solid line-c) supporting electrolyte 0.1 M PBS at pH 7.0 with a scan rate of 50 mVs^{-1}.

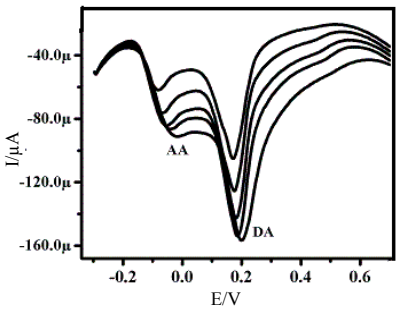

Figure 8. Differential pulse voltammograms for simultaneous determination of 0.1 mM Dopamine and 1 mL Ascorbic Acid in presence of pH 7.0 with scan rate of 50 mVs^{-1}

Resolution of DA with AA

The main goal of our present investigation was to determine the DA in presence of AA without the interference of their oxidation potentials. These two are biologically important compounds in human brain and the concentration of AA is higher than that of DA. Therefore our aim is to separate the oxidation peak potentials for AA and DA. When compared to CV, DPV has a high current sensitivity and better peak separation. DPV was used to estimate the lower limit of detection for DA and AA with the Fe-Ag CTABMCPE. Figure 8 shows the differential pulse voltammograms of DA and AA in the ranges of 1mM to 6.23mM and 1.02 mM to 7.85mM in PBS at pH 7.0. Figure 9 shows anodic peak current Vs concentration of DA and AA with a linear regressions of DA Ipa(µA)=2.283Cm ML^{-1} +0.9 and AA Ipa(µA)=1.055Cm ML^{-1} +0.7. The co-relation co-efficient of these two linear graphs were 0.9953 and 0.9952 respectively. This result shows that there was no interference of DA with AA and the peaks were resolved individually. Hence it is evident that Fe-Ag CTABMCPE can act as a good electrochemical sensor for the determination of important neurotransmitters.

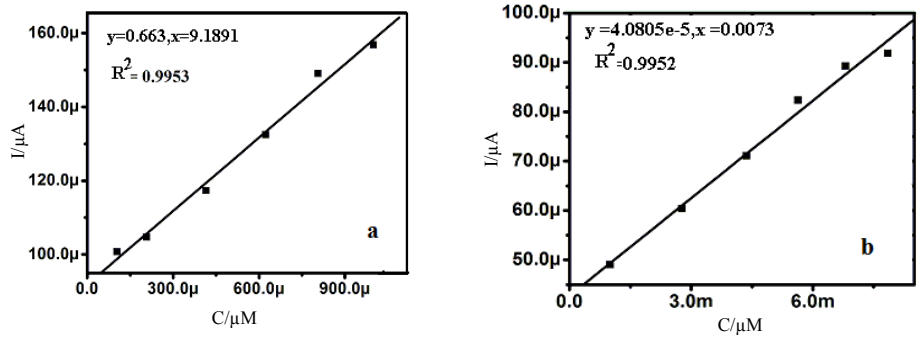

Figure 9. Differential pulse voltammograms at the Fe-Ag CTABMCPE for DA and AA with different concentrations of DA in 0.1 M phosphate buffer solution of pH 7.0

Analytical application

In order to verify the validity of the Fe-Ag MCPE for quantitative determination of DA, human serum and blood samples (obtained from the Health Centre, Sri Venkateswara University, Tirupati, Andhra Pradesh, India) were analyzed. The DA injection was purchased from Neon Laboratories India Private Ltd., with a specified content of 20.0 mg/mL. Procedure followed was: 2 mL of human serum sample without any pretreatment was diluted to 100 mL with pH 7.0 in 0.1 M phosphate buffer solution. Different volumes of this solution were mixed with a known concentration of DA solution. Similarly, a drug injection sample containing 200 mg of dopamine hydrochloride in 5 mL sterilized water was suitably diluted to provide different known standard concentrations of DA and was analyzed by DPV using the Fe-Ag MCPE as shown in Table 1. The injection of DA was analyzed by using a calibration plot. The recovery and relative standard deviation (RSD) were acceptable (n=5), in the range of 89-98% showing that the developed method could be very efficient, reliable and sensitive for the determination of DA in DA injections.

Table 1. Determination of dopamine in human serum and dopamine hydrochloride injection (n=5)

Samples	Spiked, mM	Founded, mM	Recovery, %	RSD, %
Human Serum	0.1	0.088	89%	4.8
	0.2	0.09	90%	5.5
	0.3	0.17	92%	3.2
Drug injection	0.1	0.09	90%	5.5
	0.2	0.16	94%	3.1
	0.3	0.19	98%	2.5

Conclusion

A novel method is designed for the synthesis of Fe-Ag bimetallic nanoparticles which are uniformly deposited and surface modified with CTAB on the carbon paste electrode. The modified electrode strongly enhanced both the anodic and cathodic peak current, promotes DA and AA oxidation with good enhancement when compared with bare carbon paste electrode at physiological *i.e*., pH 7.0. Obtained results of differential pulse voltammetry showed that DA does not interfere with AA detection and both could be simultaneously detected. The proposed method is also used for the detection of DA in the pharmaceutical and biological samples with satisfactory results. Therefore, the successful application of Fe-Ag modified electrode provides good sensitivity, selectivity, reproducibility and act as a low cost electro chemical biosensor.

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