

Full Paper

Simultaneous Determination of Dopamine, Acetaminophen and Xanthine by Modified Carbon Ceramic Micro-Electrode with Nanosized LaFe_{0.2}Ni_{0.8}O₃ Perovskite

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Abstract- For the first time a cheap and simple modified carbon ceramic micro-electrode (MCCME) with nanosized LaFe_{0.2}Ni_{0.8}O₃ perovskite has been developed for simultaneous determination of dopamine (DA), acetaminophen (AC) and xanthine (XN). The electrochemical response characteristics of the MCCME toward DA, AC and XN were investigated by cyclic voltammetry, differential pulse voltammetry and chronoamperometry. Under the optimum conditions, linear calibration plot was obtained over the range 6.66-131, 9.99-131 and 3.99-115 μ M with detection limits 2.1, 3.2 and 1.3 μ M for DA, AC and XN, respectively. The value of diffusion coefficient was found to be 9×10^{-6} , 6.3×10^{-5} and 4.8×10^{-4} cm^2s^{-1} for DA, AC and XN, respectively. The analytical performance of this sensor has been evaluated for simultaneous detection of these three analytes in human serum samples.

Keywords- Simultaneous determination, Carbon ceramic micro-electrode, Nanosized LaFe_{0.2}Ni_{0.8}O₃ perovskite

1. INTRODUCTION

Dopamine (3-Hydroxy tryaminium chloride, DA) is one of the excitatory neurotransmitters in mammalian central nervous system that play an important role in the

function of central nervous, renal, hormonal and cardiovascular systems [1,2]. Low concentrations of DA may cause neurological disorders such as schizophrenia and Parkinson's disease [2,3]. Acetaminophen, (N-acetyl-p-aminophenol, AC), is extensively used to prevent or reduce fever and pain drug, It has low perniciousness when used at recommended doses [4]. AC is of application for the sedation of postoperative pain as well as mild to moderate pain associated with headache, lumbago and arthritis. It is also used to reduce fevers of bacterial or viral origin. Moreover, it is known that the drug overdoses will disease liver and kidney damages [5,6]. Xanthine (3,7-dihydro-purine-2,6-dione, XN) is a purine base found in most human body tissues and fluids and in other organisms, The concentration amount of XN in biological fluids may put out sensitive indicators of specific pathologic states, especially for xanthinuria. It is a scarce genetic disorder where the lack of xanthine oxidase leads to great concentration of XN in body fluids and can cause health problems such as renal failure [7,8]. Theoretically, these compounds, DA, AC, and XN co-exist in real biological fluids blood. The perovskite sort oxides have the public formula ABO_3 , with A representing a large cation, usually rare earth ion, while B is the smaller one [9]. They are excellent nano-materials that can enhance the catalytic performance and construct highly sensitive sensors [10]. Sol-gel technology involves the manufacturing of material through the low temperature hydrolysis of a suitable monomeric precursor followed by condensation and polycondensation to yield a polymeric oxo-bridged SiO_2 network. In 1994, Lev and co-workers introduced the sol-gel-derived carbon-ceramic electrode (CCE) that comprised dispersion of carbon powder into the starting sol-gel solution [11]. CCEs have the advantages of low cost, high stability, good surface-renewal repeatability, and simplicity of preparation and modification [12]. To the best of our knowledge, there is no report on the application of modified CCE with perovskite $LaFe_{0.2}Ni_{0.8}O_3$ for simultaneous determination of DA, AC and XN. In this study, a modified carbon ceramic electrode with nanosized $LaFe_{0.2}Ni_{0.8}O_3$ perovskite is described for simultaneous determination of DA, AC and XN. The electrochemical behaviour of this modified electrode has been studied in phosphate buffer solutions (PBS) pH=3. The voltammetric peaks of DA, AC and XN were well-resolved at the modified carbon ceramic electrode. Low detection limits and high sensitivity for these three were obtained due to the high electrocatalytic properties of nanosized $LaFe_{0.2}Ni_{0.8}O_3$ perovskite. Finally, this sensor has been used successfully for the determination of these compounds in human serum.

2. EXPERIMENTAL

2.1. Reagent and materials

Methyltrimethoxysilane (MTMOS) was bought from Fluka and used without further purification. Methanol, ethanol, octanoic acid, hydrochloric acid, sodium hydroxide,

potassium chloride, ferric chloride, nickel chloride, lanthanum chloride, phosphoric acid, potassium ferrocyanide and potassium ferricyanide, provided by Merck. DA, AC and XN were obtained from Sigma Aldrich, high purity graphite powder, wall thickness, Phosphate buffer solutions (PBS) were prepared from H_3PO_4 (0.1 M). We adjusted the pH range to 2–7 with 0.1 M H_3PO_4 and NaOH solutions and used the solutions as supporting electrolytes. All solutions were prepared with doubly distilled water (DDW). Fresh serum samples were obtained from the Mehran Clinical Laboratory (Zahedan, Iran) without any pre-treatment.

2.2. Instrumentation

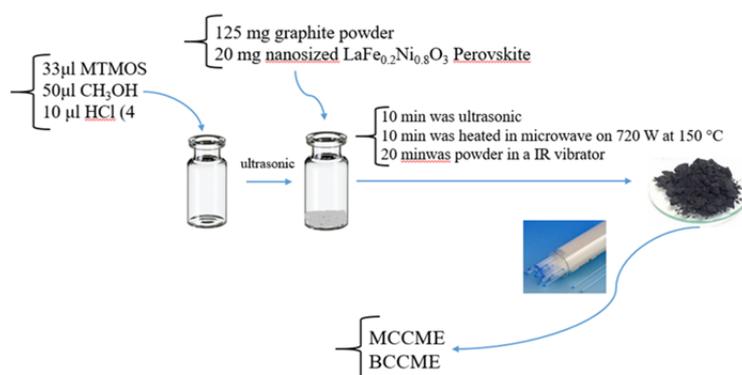
Electrochemical measurements were performed with an SAMA500 electro analyzer (SAMA Research Center, Iran). All electrochemical experiments were carried out in a conventional three-electrode cell at room temperature. A platinum electrode and a silver chloride electrode (Ag/AgCl) were used as the counter and reference electrodes, respectively. A MCCME with nanosized $\text{LaFe}_{0.2}\text{Ni}_{0.8}\text{O}_3$ perovskite was used as working electrode. Ultrasonic 4D Euronda brands and Electric furnaces model F11L1250 were used. A Metrohm pH meter, model 744 was also used for pH measurements. X-ray powder diffraction (XRD) analysis was conducted on a Philips analytical PC-APD X-ray diffractometer with graphite monochromatic CuK_α radiation ($\lambda=1.54 \text{ \AA}$) to verify the formation of products. The surface morphology and the status of the sample were observed with scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) analysis, which was equipped with an SEM instrument (SEM-Philips XL30).

2.3. Preparation of nanosized $\text{LaFe}_{0.2}\text{Ni}_{0.8}\text{O}_3$ nanocrystalline

Aqueous solutions of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{NiCl}_2 \cdot 7\text{H}_2\text{O}$ and $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$ were prepared and mixed together with different molar ratio of Fe:Ni (1:4). DDW was employed as the solvent in order to avoid the production of impurities in the resulted product. 2 mL commercial octanoic acid was added to the mixture as a surfactant. The solution was stirred followed by adding NaOH (1.5 M) drop wise to keep the pH at 7-8. After complete precipitation, the suspension was irradiated with ultrasonic waves. The sonication of 30 min / 60 °C (300 W and 40 kHz) was found to be effective in the formation of the crystalline phase of nanoparticle. After cooling at room temperature, the resulting products were centrifuged for 15 min at 403 RCF and washed with DDW and ethanol several times to remove the excess surfactant from the solution and then, were dried at 100 °C for 2 h in oven. The product was calcinated at 1000 °C for 5 h in Electric furnaces to let the product self-ignite and to burn off the organic compound in the material. The purified products $\text{LaFe}_{0.2}\text{Ni}_{0.8}\text{O}_3$ were cooled down at room temperature.

2.4. Preparation of MCCME with nanosized $\text{LaNi}_{0.2}\text{Fe}_{0.8}\text{O}_3$ perovskite

The MCCME with nanosized $\text{LaNi}_{0.2}\text{Fe}_{0.8}\text{O}_3$ perovskite (MCCME-LaNiFe) was prepared according to the procedure previously described for sol-gel carbon ceramic electrode by microwave irradiation by Abbaspour and Ghaffarinejad with a minor modification [13] with adding nanosized $\text{LaFe}_{0.2}\text{Ni}_{0.8}\text{O}_3$ perovskite. MTMOS (33 μl), CH_3OH (50 μl), and 10 μl HCl (4 mol/L) were mixed in ultrasonic bath for 5 min until a homogeneous gel solution appeared. Then 125 mg graphite powder and 20 mg nanosized $\text{LaFe}_{0.2}\text{Ni}_{0.8}\text{O}_3$ perovskite were added, and the resulting mixture was ultrasonic for an additional 10 min, then the mixture was heated in microwave on 720 W at 150 $^\circ\text{C}$ for 10 minutes and then was powdered in an IR vibrator for 20 minutes. The mixture was packed in a micro-hematocrit tube with inner diameter and length (0.11 cm \times 12 cm) and a copper wire was inserted into the MCCME as an electrical contact. The bare carbon ceramic electrode was made by the same procedure but without adding the perovskite. Then the electrode was placed in 0.1 M NaOH and the electrode potential was cycled between 0 and 1 V (*vs.* Ag/AgCl) at a scan rate of 50 mVs^{-1} for 15 cycles in a cyclic voltammetry regime until a stable voltammogram was obtained. The process for making electrodes of MCCME-LaNiFe and BCCME was shown in schematic 1.



Scheme 1. The process for making electrodes of MCCME and BCCME

3. RESULTS AND DISCUSSION

3.1. Characterization of $\text{LaFe}_{0.2}\text{Ni}_{0.8}\text{O}_3$ nanocrystals

X-ray diffraction pattern of synthesized materials in this study is depicted in Figure 1. In Fig. 1A, the XRD analysis of $\text{LaNi}_{0.2}\text{Fe}_{0.8}\text{O}_3$ nanocrystal showed the pattern corresponding to JCPDS File no: 21-0972, which crystallizes in the orthorhombic system with a main diffraction peak at $d=2.90$ Å ((1 7 1) plane). Elemental composition of the surface of the perovskites were estimated using EDX and have been showed in Fig. 1B. The presence of lanthanum, oxygen, iron and nickel as the only component elements were observed. To investigate the morphology and size of the particles, scanning electron microscopy (SEM) was also used. The SEM image of the particles is shown in Fig. 1C. The mean size of sphere

like $\text{LaNi}_{0.2}\text{Fe}_{0.8}\text{O}_3$, nanoparticles was approximately 43 nm. The SEM images show that there were some small holes inside the products, which indicates that they may be used in catalysis. Furthermore, in the SEM images, the presence of holes confirms the porosity of synthesized perovskites.

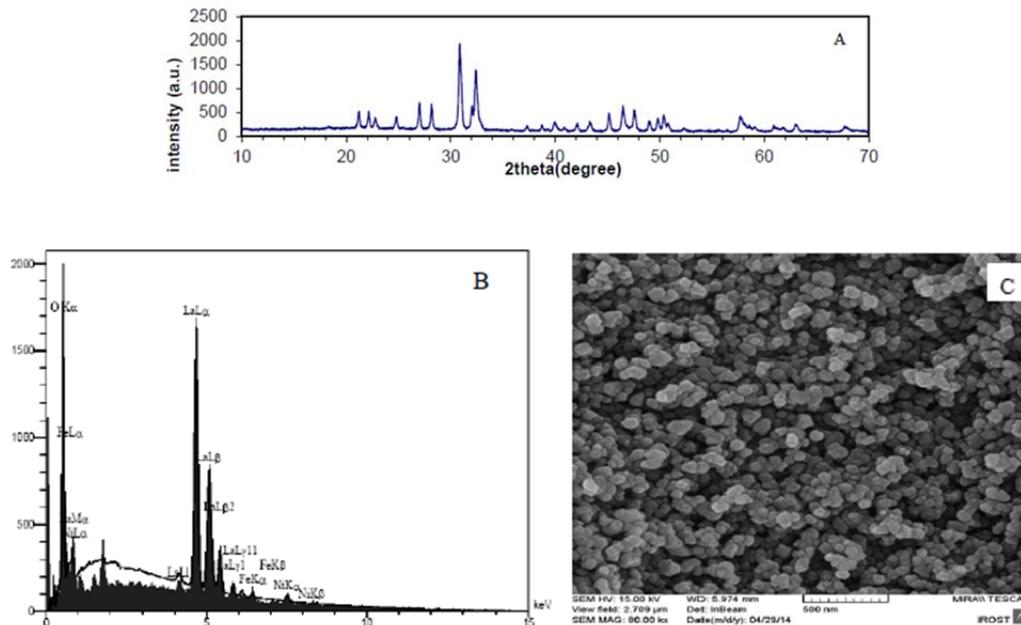


Fig. 1. (A) XRD pattern; (B) EDX and (C) SEM of nanocrystalline $\text{LaFe}_{0.2}\text{Ni}_{0.8}\text{O}_3$

3.2. Electrochemical properties of modified carbon ceramic micro-electrode with nanosized $\text{LaNi}_{0.2}\text{Fe}_{0.8}\text{O}_3$ perovskite

The electrochemical properties of MCCME-LaNiFe were studied by cyclic voltammetry. Electrochemical measurements of the MCCME-LaNiFe and bare CCME (BCCME) were analyzed for the anodic peak current (I_{pa}) of the respective cyclic voltammograms obtained in the presence of 1 mM of $\text{Fe}(\text{CN})_6^{3-/4-}$ as the electrochemical probe in KCl 0.1 M as supporting electrolyte. Fig. 2A-B shows the cyclic voltammograms of BCCME and MCCME-LaNiFe at various scan rates, respectively. Based on the Randles-Sevcik equation [14]:

$$I_{pa} = 2.69 \times 10^5 n^{3/2} A C_0 D_R^{1/2} v^{1/2} \quad (1)$$

Where I_{pa} refers to the anodic peak current, n is the electron transfer number, A is the surface area of the electrode, D_R is the diffusion coefficient, C_0 is the concentration of $\text{K}_3\text{Fe}(\text{CN})_6$ and v is the scan rate. For 1 mM $\text{K}_3\text{Fe}(\text{CN})_6$ in the 0.1 M KCl electrolyte, $n=1$ and $D_R=7.6 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$; the microscopic areas were calculated from the slope of the $I_{pa}-v^{1/2}$ relation (Fig. 2C). For BCCME and MCCME-LaNiFe, the electrode were found to be 0.46 and 0.29 cm^2 , respectively. Therefore, the results indicated the presence of LaNiFe, greatly

improved the effective area of the electrode and cooperate to increase the conductivity of the sensor. Fig 3 showed the cyclic voltammograms were obtained in the PBS at BCCME and MCCME-LaNiFe. At the MCCME-LaNiFe the field current is higher than the BCCME. Based on this figure the charge transfer of MCCME-LaNiFe is more than BCCME.

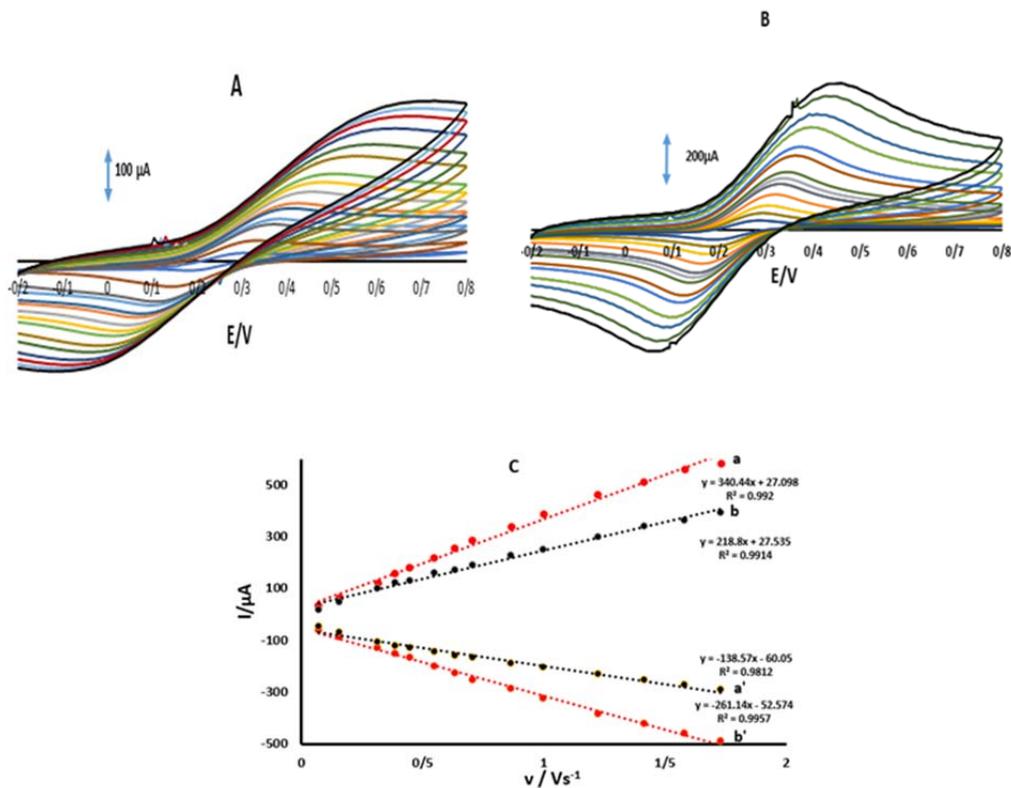


Fig. 2. (A) and (B) Cyclic voltammograms of BCCME and MCCME-LaNiFe in the presence of 1.0 mM of $\text{Fe}(\text{CN})_6^{3-/4-}$ in KCl 0.1 M of supporting electrolyte, at various scan rate: 5, 10, 25, 50, 75, 100, 200, 300, 400, 500, 750, 1000, 1500, 2000 mV/s; (B) Plots of anodic and cathodic peak current of MCCME-LaNiFe (a,d) and BCCME (b,c)

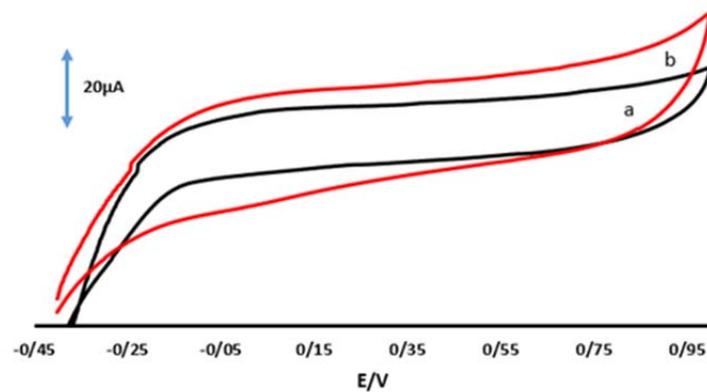


Fig. 3. (a) Cyclic voltammograms of MCCME-LaNiFe and (b) BCCME obtained in pH=3 PBS

3.3. Electrocatalytic oxidation of DA, AC and XN

Fig. 4A depicts the electrochemical behaviors of the mixed components of DA, AC and XN at MCCME-LaNiFe and BCCME in the potential range 0.2 -1.2 V/ Ag/AgCl and in 0.1 M PBS of pH=3. Based on this Figure, BCCE showed three weak peaks at potential of 0.48, 0.66 and 0.98 V. The behavior of MCCME-LaNiFe showed three well-defined and sharp peaks for DA, AC and XN at 0.49, 0.65 and 1.02 V. Also DPVs of DA, AC and XN as a mixture and individual solution in the same potential range were shown in Fig. 4B, Based on this Figure, the oxidation potential peaks of analytes in the mixture and individual solution are constant.

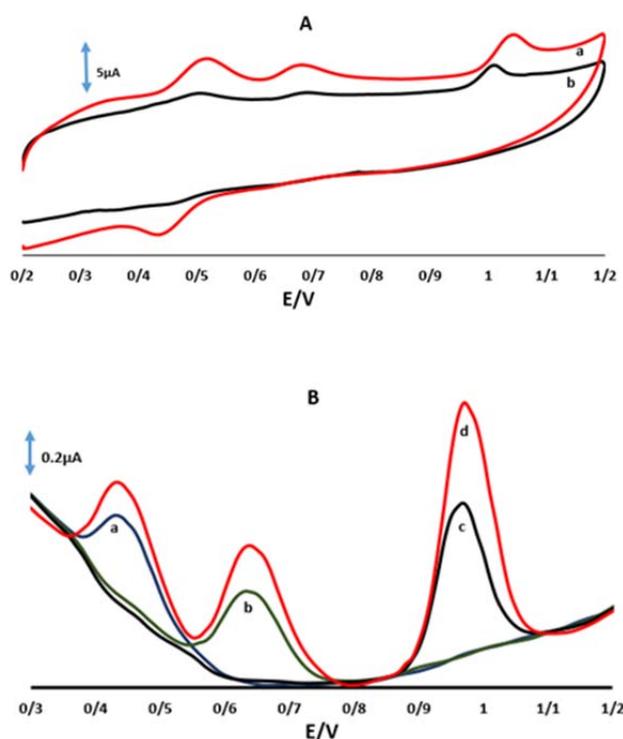


Fig. 4. (A) A comparison electrochemical behaviour study of 33.2 μM DA, AC and XN at (a) MCCME-LaNiFe and (b) BCCME; (B) DPVs of DA, AC and XN of the individual solution of 16.6 μM DA (a), 16.6 μM AC (b), 23.3 μM XN (c) and 40 μM DA, 40 μM AC, 50 μM XN in their mixture (d) in the same potential range and at pH=3 at MCCME-LaNiFe

3.4. pH effect

Fig. 5 showed the effect of pH on MCCME-LaNiFe of 9.99 μM DA, 49.7 μM AC and 49.7 μM XN in PBS at the range of 2–7. Maximum of currents are at pH=3. The potentials of DA, AC and XN followed the linear regression equations with pH: $E_{\text{pa}}(\text{DA}) = -0.062 \text{ pH} + 0.377$ ($R=0.997$), $E_{\text{pa}}(\text{AC}) = -0.059 \text{ pH} + 0.8364$ ($R=0.9987$) and $E_{\text{pa}}(\text{XN}) = -0.065 \text{ pH} + 1.2172$ ($R=0.9979$) respectively. Regarding the observed slopes of 0.062, 0.059 and

0.065 mV/pH for DA, AC and XN which was close to the anticipated Nernstian value for a two-electron, two-proton electrochemical reaction [15]. An electrochemical reaction of DA, AC and XN at the surface of MCCME-LaNiFe are illustrated in eqs. (2)-(4), respectively.

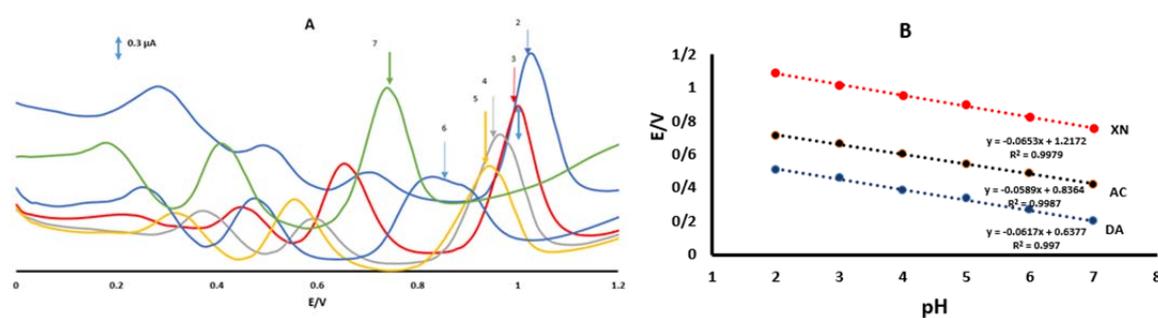
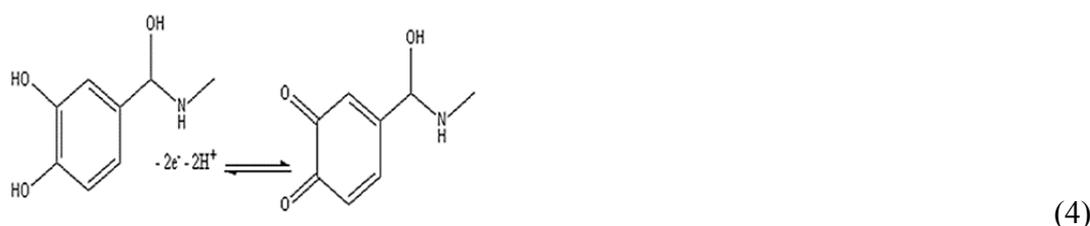


Fig. 5. (A) DPVs of 9.99 μM DA, 49.7 μM AC and 49.7 μM XN at MCCME-LaNiFe at pH 2 to 7; (B) Plots of peak potential versus pH for DA, AC and XN

3.5. Chronoamperometric

Chronoamperometric measurements of DA, AC and XN at the MCCME-LaNiFe were done by setting the working electrode potential at 0.45, 0.65 and 1.0 V and used for the measurement of the diffusion coefficient DA, AC and XN, respectively. Fig. 6A was shown a typical chronoamperograms for DA. According to Cottrell equation [16], for an electro active material with a diffusion coefficient, the current for the electrochemical reaction (at a mass transport limited rate) is explained by the following equation:

$$I = n F A D^{1/2} C \pi^{-1/2} t^{-1/2} \quad (5)$$

Where D and C are the diffusion coefficient (cm^2s^{-1}) and the concentration ($\text{mol}\cdot\text{cm}^{-3}$), respectively. On the other hand, A and F are the surface area of the working electrode ($1.69 \times 10^{-4} \text{ cm}^2$) and Faraday constant ($96,485 \text{ C mol}^{-1}$), respectively. Under diffusion control (mass transport), a plot of I vs. $t^{-1/2}$ is linear (Fig. 6B), and the value of D can be obtained from its slope. The value of D was found to be 9×10^{-6} , 6.3×10^{-5} and $4.8 \times 10^{-4} \text{ cm}^2 \text{ s}^{-1}$ for DA, AC and XN, respectively.

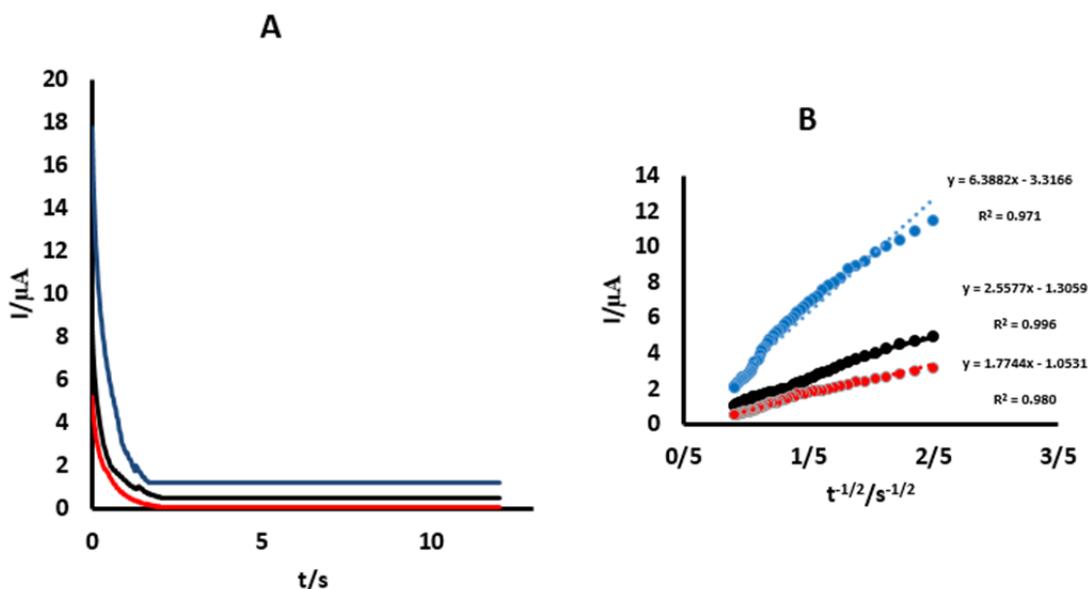


Fig. 6. (A) A typical chronoamperograms obtained at MCCME-LaNiFe at pH=3 for different concentrations 0.1, 0.5 and 1 mM of DA; (B) Plots of I vs. $t^{-1/2}$ obtained from chronoamperograms DA

3.6. Simultaneous determination of DA, AC and XN

DPV was used for simultaneous determination of DA, AC and XN. Fig. 7A has shown the oxidation peak currents of DA, AC and XN at MCCME-LaNiFe. Fig. 7B show a linear regression equation between the oxidation peak current with the concentration of DA was obtained: $I_p = 0.0109[\text{DA}] + 0.2378$ (I_p in μA , C in μM and $R^2 = 0.9865$), with over the range 6.66-131 μM . The detection limit for DA was calculated (using $DL = 3S_{\text{bk}}/m$, S_{bk} and m are the standard deviation and slopes of calibration curve, respectively) to be 2.1 μM . Fig. 7C shows the linear regression equation of AC was obtained: $I_p = .008[\text{AC}] + 0.2774$ (I_p in μA , C in μM) ($R^2 = 0.9889$), with over the range 9.99-131 μM with a detection limit 3.2 μM , and Fig. 7D shows the linear regression equation of XN was: $I_p = 0.0274[\text{XN}] + 0.0103$ (I_p in μA , C in μM) ($R^2 = 0.9912$), with over the range 3.99-115 μM and the detection limit for XN was 1.3 μM .

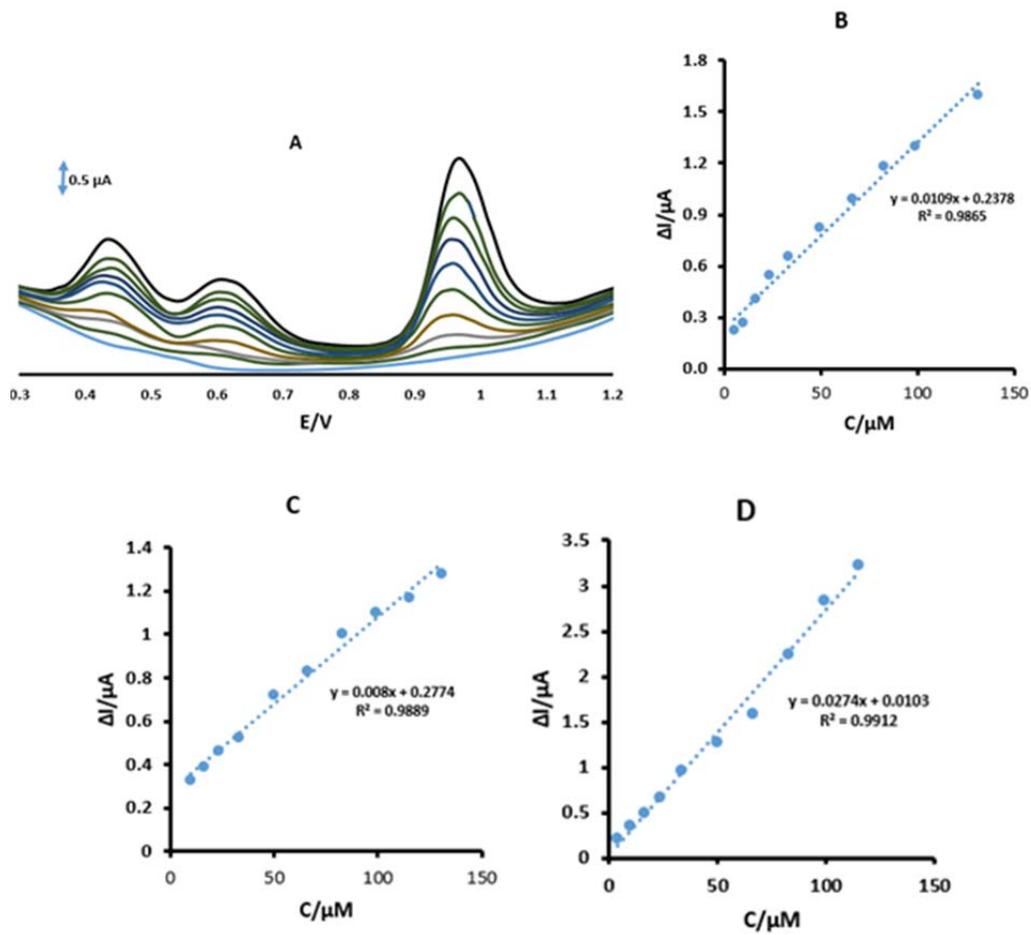


Fig. 7. (A) DPVs of MCCME-LaNiFe at pH=3 containing different concentrations of the mixtures of DA, AC and XN. Plots of I_p vs. concentration for (B) 4.99, 9.99, 16.6, 23.3, 33.2, 49.7, 66.2, 82.6, 99, 131 μM of DA, (C) 9.99, 16.6, 23.3, 33.2, 49.7, 66.2, 82.6, 99, 115, 131 μM of AC and (E) 3.99, 9.99, 16.6, 23.3, 33.2, 49.7, 66.2, 82.6, 99, 115 μM of XN

3.7. Interference effect

For the interference study, the concentration of one species changed, while the concentrations of the other one were kept constant. Fig. 8A showed the DPVs of $\text{LaFe}_{0.2}\text{Ni}_{0.8}\text{O}_3/\text{CCE}$ in the presence of 9.99 μM AC and 3.99 μM XN and different concentrations of DA, and Fig. 8B showed the DPVs in the presence of 4.99 μM DA and 3.99 μM XN and different concentrations of AC. Finally, the Fig. 8C showed the in the presence of 20 μM DA and 9.99 μM AC and different concentrations of XN. As it can be seen from Fig. 8, the DPVs corresponding to the oxidation of DA or AC or XN were found to increase linearly in consonance with the increase in their concentration, whereas the peak current for the oxidation of other two compounds remain constant. So, they do not interfere in the determination of each other.

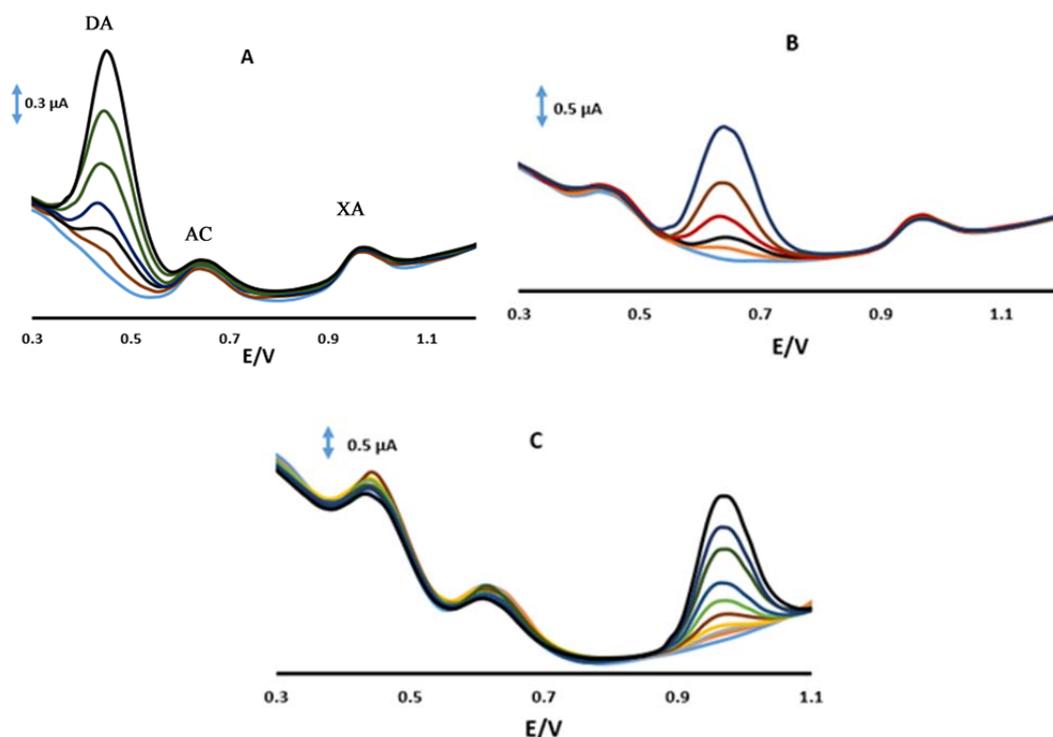


Fig. 8. (A) DPVs of MCCME-LaNiFe at pH=3 in the presence of (A) 9.99 μM AC and 3.99 μM XN, containing different concentrations of DA, Inset: 0, 4.99, 9.99, 23.3, 66.2, 82.6, 131 μM ; (B) in the presence of (B) 4.99 μM DA and 3.99 μM XN, containing different concentrations of AC, Inset: 0, 9.99, 16.6, 33.2, 66.2, 131 μM ; (C) in the presence of 20 μM DA and 9.99 μM AC, containing different concentrations of XN, Inset: 0, 3.99, 4.99, 9.99, 16.6, 23.3, 33.2, 66.2, 79.1, 86.1 μM

3.8. Real Sample Analysis

To evaluate the practical application of MCCME-LaNiFe for human serum sample analysis, three kinds of human serum samples were detected.

Table 1. The application of MCCME-LaNiFe for simultaneous determination of DA, AC and XN in human blood serum, (n=3)

Sample	Spiked (μM)			Found (μM)			Recovery (μM)			RSD* (%)		
	DA	AC	XN	DA	AC	XN	DA	AC	XN	DA	AC	XN
Serum 1	0	0	0	ND**	ND	ND	-	-	-	-	-	-
	33	33	33	32.6	33.4	32.8	98.7	101.2	99.3	1.7	1.18	2.14
	99	99	99	98.1	101.3	98.4	99.0	102.3	99.4	1.56	1.96	2.43
	131	131	131	133.2	128.4	130.7	101.7	98.0	99.8	2.12	2.32	1.92
Serum 2	0	0	0	ND	ND	ND	-	-	-	-	-	-
	33	33	33	33.2	33.1	32.5	100.6	97.3	98.4	1.65	2.48	1.63
	99	99	99	100.4	101.7	102.1	101.4	102.7	103.2	1.96	1.43	2.23
	131	131	131	127.8	132.1	134.2	97.5	100.8	102.4	2.53	1.77	1.94

*RSD relative standard deviation, **ND not detected

The calibration samples were analyzed by adding the concentration of determined sample by sample with DPV. As show in Table1, the recoveries of three human serum samples were 97.5–101.7% for DA, 98.0–102.7% for AC and 99.4–103.1% for XN respectively, indicating practical applicability and reliability of MCCME-LaNiFe for simultaneous determination of DA, AC and XN in practice real samples.

3.9. Stability and reproducibility

The stability and reproducibility of MCCME-LaNiFe were investigated. DPV response for 33.2 μM DA, 33.2 μM AC and 82.6 μM XN at pH =3 at MCCME-LaNiFe was shown in Fig. 9. The relative standard deviation (RSD (%)) for DA, AC and XN were 0.32 (%), 0.37 (%) and 0.15 (%), respectively. Therefore, MCCME-LaNiFe has an excellent stability and reproducibility.

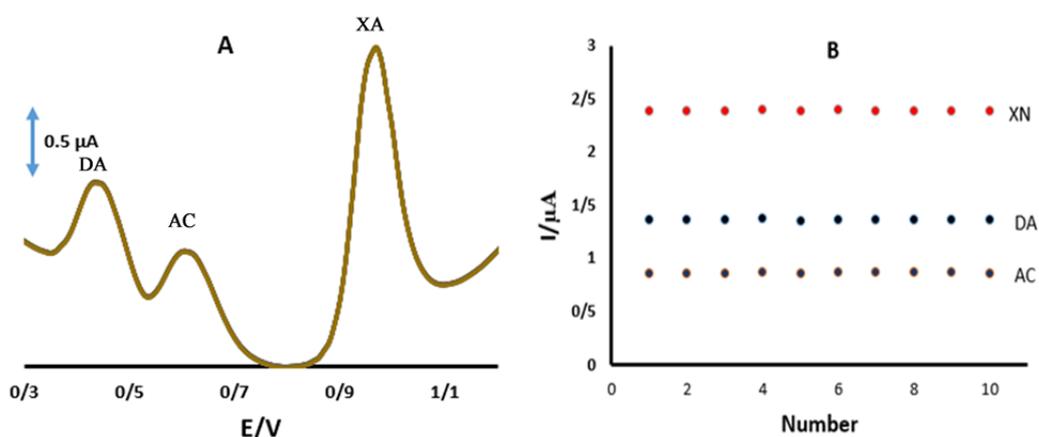


Fig. 9. The stability of repetitive measurements of DPV response in the presence of 33.2 μM DA, 33.2 μM AC and 82.6 μM XN at pH=3 at MCCME-LaNiFe

4. CONCLUSION

In this study, a sensitive and reliable electrochemical platform was designed for simultaneous determination of DA, AC and XN by MCCME with LaNiFe. Under optimum condition, the modified electrode showed a detection limits 2.1, 3.2 and 1.3 μM for DA, AC, and XN, respectively. The diffusion coefficients were found to be 9×10^{-6} , 6.3×10^{-5} and $4.8 \times 10^{-4} \text{ cm}^2 \text{ s}^{-1}$ for DA, AC and XN. The recoveries of two human serum samples were 97.5–101.7% for DA, 98.0–102.7% for AC and 99.4–103.1% for XN, respectively. Finally, the proposed modified electrode has been used for simultaneous determination of DA, AC and XN in real samples.

Acknowledgments

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