Full Paper

Synthesis, Characterization of Calcium Ferrite Nanoparticles and their Modified Carbon Paste Electrode for the Electrochemical Investigation of Dopamine in Presence of Uric Acid and Folic Acid

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Abstract- Calcium ferrite nanoparticles ($CaFe_2O_4$) were prepared by a solution based method using calcium chloride ($CaCl_2$), Ferrous sulphate ($FeSO_4$), dl serine and sodium hydroxide (NaOH) as a precipitant and the obtained precipitation was calcinated under 500 $^\circ$C for 4 h. The resulting material was characterized by using X-ray diffractometry (XRD), Energy dispersive spectroscopy (EDS) and Scanning electron microscopy (SEM). The $CaFe_2O_4$ NPs were used for the preparation of $CaFe_2O_4$ NPs/carbon paste electrode ($CaFe_2O_4$ NPs/CPE) and applied for the electrochemical investigation of dopamine (DA), uric acid (UA) and folic acid (FA) which exhibits good electrocatalytic activity for investigation of DA, UA and FA at physiological pH 7.4. The electrocatalytic currents increased linearly with an increase in DA, UA and FA concentration and the scan rate effect was studied. The modified electrode shows, overall electrode process is adsorption and diffusion controlled.

Keywords- Calcium ferrite nanoparticles, Carbon paste electrode, Cyclic voltammetry, Dopamine, Uric acid and folic acid

1. INTRODUCTION

Recent studies have been focused on nanoferrites as electrocatalysts for many organic and inorganic reactions. Nanoferrites have been prepared solution based method and their structural and magnetic properties have been elucidated [1–4]. Ca–Fe–O is one of the interesting systems, which finds application as oxidation catalysts, high-temperature sensors, gas absorbers, electrodes for solid oxide fuel cells etc. [5–7]. $CaFe_2O_4$ is used as pigment [8], as an anode material in lithium batteries [9] and employed as catalytic material [10]. $CaFe_2O_4$ has been synthesized using various methods such as ceramic method [10], Pechini process [11] and co-precipitation method [12]. A novel synthesis route for both calcium ferrites ($CaFe_2O_4$ and $Ca_2Fe_2O_5$) was proposed [13] using mechanically activated mixtures of organic precursors. It is prepared by mechanical activation using a mixture of $Ca(OH)_2$/a-FeOOH [14] and by thermal decomposition of $Ca[Fe(CN)_5NO] 4H_2O$ [15]. A co-precipitation method $CaFe_2O_4$ NPs has been reported in previous literature [16] and the prepared NPs was modified and used as the electrochemical sensor for the detection of DA in the presence of UA and FA. In the present work, this manuscript discusses the synthesis of $CaFe_2O_4$ nano crystalline by solution based method and their electro catalytic behavior towards DA, UA and FA was studied.

The dopamine (DA), uric acid (UA) and folic acid (FA) are compounds of great biomedical interest, playing a potential role in human metabolism. DA is one of the most important neurotransmitters and is present in the mammalian nervous system. It is catecholamine in the form of a large organic cations and belonging to the family of excitatory chemical neurotransmitters [17]. In a healthy human being, the typical concentration of DA is around $50 nmolg^{-1}$ when change in this concentration body may causes diseases (Abnormalities). Determination of DA has become important tremendous attention by neuroscientists and chemists in biomedical and bioanalytical research since its discovery during the 1950 s. DA possesses high electrochemical activity and has been widely studied by electroanalytical techniques to significantly benefit biosciences [18,19-21]. Detection of DA in the physiological environment with sensitivity has been an important role of electroanalytical research. It is well known that detection of DA directly with commercial available electrodes, such as carbon and metallic electrodes is ineffective. Therefore it is important to establish a fast, sensitive method for the detection of DA by the modification of bare electrodes and makes their detection possible by electrochemical methods based on anodic oxidation [22].

Uric acid (UA) is the primary end product of purine metabolism in the human body [23]. In a healthy human being, the typical concentration of UA in urine is around 2 mM and in the blood is in between 120 μM to 450 μM ranges [24,25]. Extreme abnormalities of UA levels are symp-tomic of several diseases, such as, cardiovascular disease [26], hyperuricaemia, uric acid stones [27], gout and Le-seh-Nyhan syndrome [28]. Thus accurate determination of UA

concentration is of great importance. Recently, electrochemical sensors have attracted much attention due to their advantages of simplicity, cheapness, fast analysis along with high sensitivity and selectivity [29].

Folic acid (FA) is a component of considerable biological importance [30]. It has long been recognized as part of the vitamin B complex. It appears to be one of the important elements of the haemapoietic system and is the coenzyme that controls the generation of ferrohaeme. A lack of folic acid gives rise to gigantocytic anaemia, associated with leukopaenia, devolution of mentality, psychosis etc. Determination of FA is often required in pharmaceutical, clinical and food samples. Methods used for it are generally spectrophotometry [31] and chromatography [32,33].

The proposed NPs are used for the simultaneous determination of DA, UA and FA using $CaFe_2O_4$ NPs/CPE modified carbon past electrode. Electrochemical detection of DA and AA by using $LaFeO_3$ nanoparticles, CdO nanoparticles, chemically modified carbon paste electrode [34–39] poly (Naphthol Green B) film graphite pencil electrode [40] and gold nanoparticles modified ITO electrode [41] has been reported. A simple solution based method previously reported $MgFe_2O_4$ NPs/CPE [42]. And the same method was followed for the preparation of $CaFe_2O_4$ NPs with average crystalline size 62 nm and SEM morphology shows particle like small nanograins with average size 50 nm. The $CaFe_2O_4$ NPs/CPE exhibits enhancement of current response for investigation of DA,UA and FA at pH 7.4 in 0.2 M phosphate buffer solution and the electrocatalytic current increases linearly with increase in concentration of DA,UA and FA.

2. EXPERIMENTAL PART

2.1. Reagents

Calcium chloride ($CaCl_2$) and ferrous sulphate ($FeSO_4$) were purchased from sd.fine chemicals. Ascorbic acid, sodium dihydrogen orthophosphate (NaH_2PO_4), disodium hydrogen phosphate (Na_2HPO_4) and silicon oil form Hi Media chemicals, dl serine, absolute ethanol (99.9%), Sodium hydroxide (NaOH) and graphit powder was from Merck chemicals. All other chemicals were of analytical grade. Phosphate buffer is prepared adjusting the pH 7.4 with 0.2 M NaH_2PO_4 and Na_2HPO_4 solution. All the aqueous solutions were prepared using double distilled water.

2.2. Apparatus

Voltammetric measurements were performed with a model 660 c (CH instruments) potentialstat/galvanostat. A conventional three electrode cell was used with a reference as a saturated calomel electrode (SCE), a platinum wire counter electrode and a bare or $CaFe_2O_4$ NPs/CPE modified electrode as working electrode. XRD studies using a (Model D8 Advance,

Bruker) with a Cu- Kα1 X-ray radiation (λ=0.15406 nm) diffracttometer. Structural morphology of the synthesis NPs was studied using a VEGA3 TESCAN Scanning electron microscopy (SEM).

2.3. Preparation of CaFe$_2$O$_4$ nanoparticles

The first solution 0.2 M CaCl$_2$, 0.4 M FeSO$_4$ and 0.2 M dl-Serine was dissolved in 250 mL of distilled water and the second solution was prepared by 3 M NaOH pallets in 250 mL distilled water. The second solution was added drop by drop with continues stirring on magnetic stirrer. The obtained precipitate solution was taken in the condenser and boiled at 100 °C temperature for about 2 h then the hot solution was filtered by using Whatmann filter paper (G-41) and dried at 100 °C in a hot air oven for about one hour. The dried precipitate was transferred to silica crucible and ignited at 500 °C for about four hour, then obtained powder was washed with ethanol 3-4 times to remove the impurities present in CaFe$_2$O$_4$Nps.

2.4. Preparation of bare CPE and modified CPE

The bare CPE was prepared by hand mixing of graphite powder and silicon oil at a ratio 70:30(w/w) in an agate mortar until a homogenous paste was obtained. The paste was then tightly packed into the homemade cavity and smoothed on weighing paper. The CaFe$_2$O$_4$ NPs/CPE was prepared by adding 2, 4, 6 and 8 mg CaFe$_2$O$_4$ NPs to the above mentioned graphite powder and silicon oil mixture. The electrical contact was provided by a copper wire connected to the end of the tube.

3. RESULT AND DISCUSSION

3.1. Characterization

The XRD pattern of the obtained calcium ferrite (CaFe$_2$O$_4$) Nps was show in (Fig. 1a). All the peaks can be well indexed to the hexagonal structure of calcium ferrite (JCPDS PDF, no 72-1199) with high crystalline. No impurity peaks were observed other than calcium ferrite, indicating high purity of the products and by using Debye Scherer's formula, the crystallite size of CaFe$_2$O$_4$ NPs can be determined. The obtained average particle size of the particles was 62 nm.SEM observations reveals that all the products consist of a large quantity of a small nano grains with average size around 20-50 nm, as shown in (Fig. 1b). EDS indicates that atom ratio of Ca, Fe and O about 1: 2: 3 as shown in (Fig. 1c).
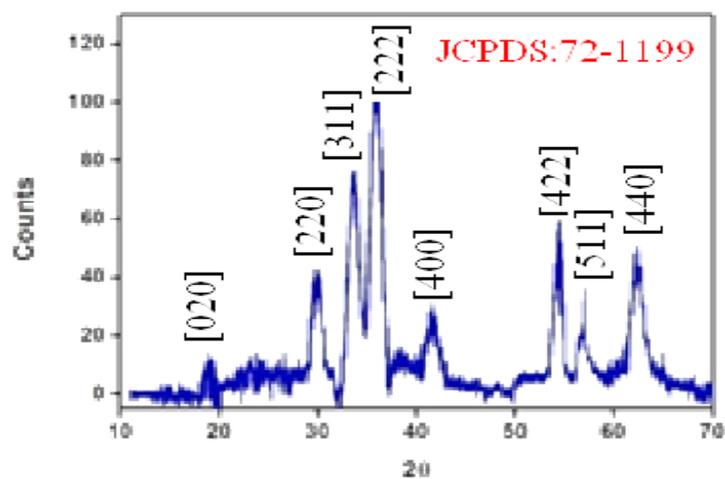
(A)
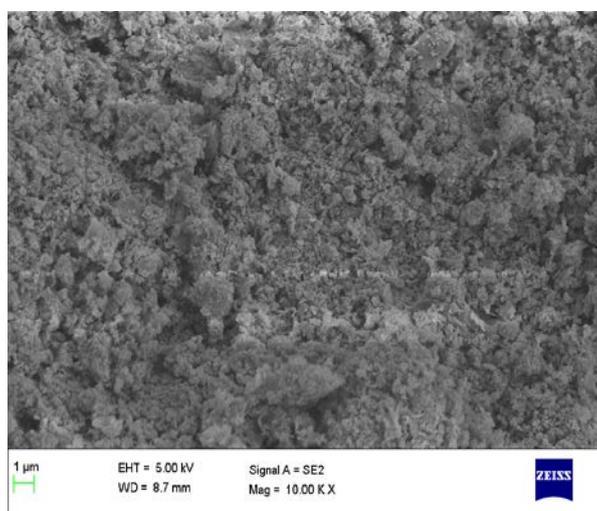
(B)
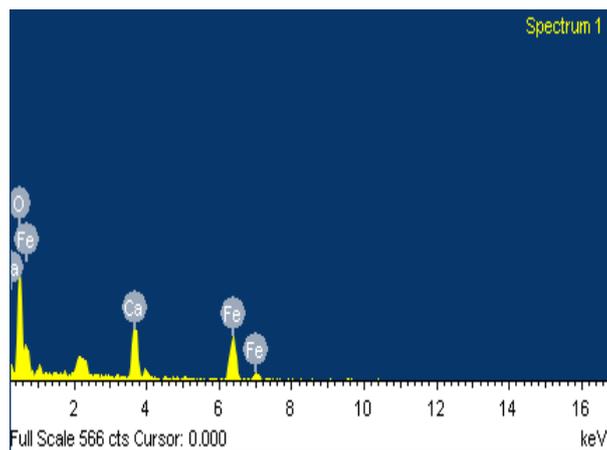
(C)

Fig. 1 (A). XRD Pattern for $CaFe_2O_4NPs$; **(B).** SEM image for $CaFe_2O_4NPs$; **(C).** EDS image for $CaFe_2O_4NPs$

3.2. Effect of CaFe$_2$O$_4$ NPs in CPE for investigation of DA

The effect of CaFe$_2$O$_4$ NPs CPE for the investigation of 1×10^{-4} M *DA* in 0.2 M phosphate buffer solution at pH 7.4 was studied by cyclic voltammetry technique. The electro chemical sensitivity of modified carbon past electrode by different (2, 4, 6 and 8 mg) weight of CaFe$_2$O$_4$ NPs was studied among them 4mg CaFe$_2$O$_4$ NPs modified CPE shows higher electro chemical sensitivity towards DA as in the Fig. 2 and this electrode was used for the further investigation.
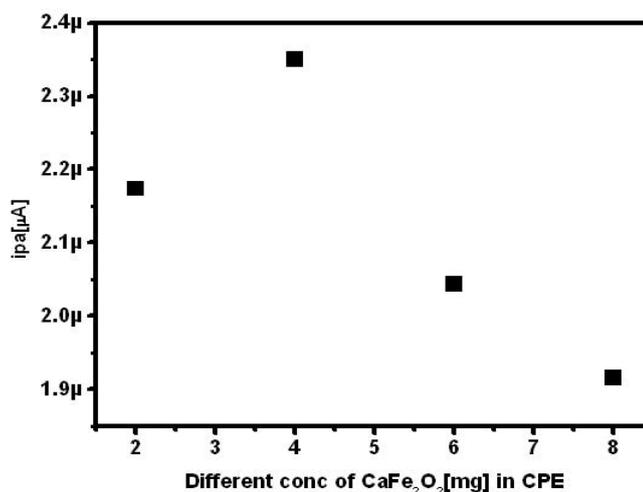

Fig. 2. Different concentration of CaFe$_2$O$_4$ NPs (mg) in CPE

3.3. The electrochemical response of DA at the bare CPE and MCPE

The electrochemical responses of 1×10^{-4} M DA in 0.2 M phosphate buffer solution of pH 7.4 at the bare carbon past electrode (BCPE) and the modified carbon past electrode prepared with the CaFe$_2$O$_4$ nanoparticles (MCPE) with the scan rate 100 mv/s is shown in (Fig. 3a). At the BCPE, the difference between anodic peak potential (Epa) 0.16 V and cathodic peak potential (Epc) 0.08 V with ΔEp 0.08 V However a well-defined redox wave of DA was observed and the peak currents significantly increased at the MCPE with the anodic peak potential shifting negatively to 0.13 V and the corresponding cathodic peak potential is 0.09 V and ΔEp is 0.04 V indicates the modified electrode shows fast electron transfer process. Compared to the bare CPE and the modified CPE remarkable enhancement in the peak currents with reduction of over potential showed electro catalytic effect of the CaFe$_2$O$_4$ nanoparticles. The mechanism could be modified CPE under the condition, CaFe$_2$O$_4$ nanoparticles may be combined with the covalent bond of the hydroxyl of DA, which activated hydroxyl, weakened the bond energy of hydroxyl and improved the electron transfer rate. At the same time, CaFe$_2$O$_4$ nanoparticles also increases the electrod area.
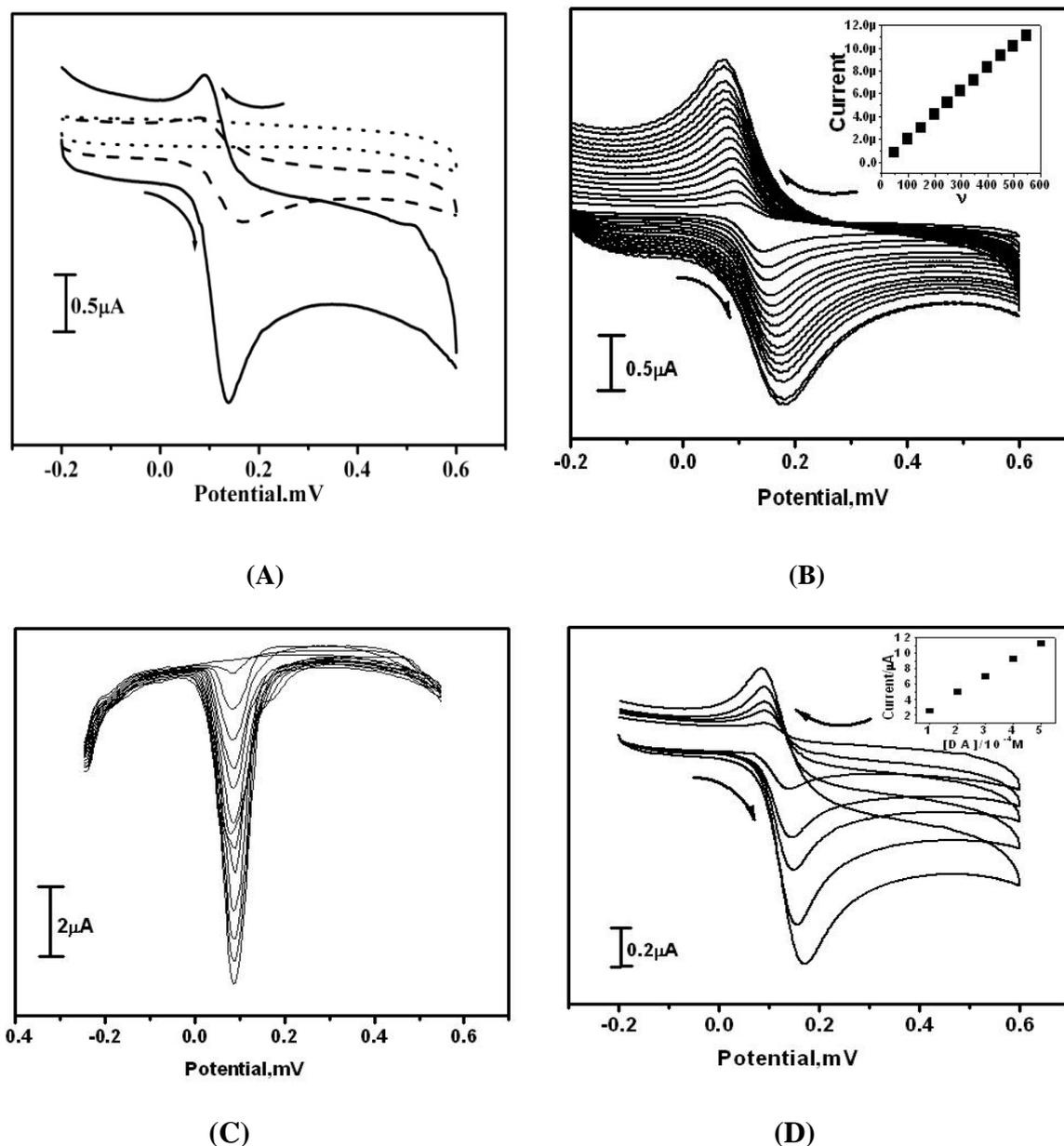
(A)

(B)

(C)

(D)

Fig. 3 (A). Cyclic voltammogram of 1×10^{-4}M DA in PBS at pH 7.4 at dotted line for blank, for dashed line bare and solid line for $CaFe_2O_4$ NPs MCPE; **(B)** Cyclic voltammograms of $CaFe_2O_4$ NPs MCPE in PBS solution pH 7.4 with different scan rate DA (100 to 800 mVs^{-1}). Inset shows the Graph of anodic peak current v/s scan rate of DA; **(C).** Differential pulse voltammogram of different concentration of DA at $CaFe_2O_4$ NPs MCPE (0.3 to 0.22 µM); **(D).** Cyclic voltammograms of $CaFe_2O_4$ NPs MCPE in PBS solution pH 7.4 with different concentration DA (1 to 5 µM). Inset shows the Graph of anodic peak current v/s concentration of DA

3.4. Effect of Scan rate

The scan rate effect for 1×10^{-4} M DA in 0.2 M PBS at pH 7.4 was studied by CV at $CaFe_2O_4$ nanoparticles MCPE as shown in (Fig. 3b). $CaFe_2O_4$ NPs/CPE showed increase in

the redox peak currents with increase in scan rate (100 to 800 mV/s). The graph of redox peak current (IPa) *vs* scan rate (ν) was plotted. The graph obtained was good linearity between scan rate and redox peak current (insert Fig. 3b) in the range from 100–800 mV/s. The correlation coefficient (r^2) was 0.9993, which indicate the electrode reaction was adsorption controlled process.

3.5. The effect of the concentration of DA

The differential pulse voltammetric technique was used for the analysis of DA concentration which was varied from 3 to 22 μM shown in (Fig. 3c) for the $CaFe_2O_4$ nanoparticles MCPE with increasing the concentration of DA from 3–22 μM. The electrocatalytic oxidation of DA was carried out by varying the concentration at MCPE (Fig. 3d) by increasing the concentration of DA from 1×10^{-4} M to 5×10^{-4} M. The graph of Ipa and Ipc goes on increasing with shifting Epa towards positive side and Epc towards negative direction slightly. The concentration showed the Epa was increased from 135 mV to 169 mV. The graph of Ipa versus concentration of DA was plotted shows increase in electrochemical peak current (insert Fig. 3d) the graph obtained linearly increase in peak current with increase in the DA concentration. The correlation coefficient were found to be 0.9991.

3.6. Electrocatalytic sensor of UA and FA at the bare CPE and MCPE

The electrochemical responses of 1×10^{-4} M UA at bare carbon paste electrode and $CaFe_2O_4$ Nps/CPE using 0.2 M phosphate buffer solution at physiological pH (7.4) and potential range from -0.2 to 0.6 V, sweep rate of 100 mVs^{-1}. From the (Fig 4a) peak current of UA at a bare carbon paste electrode was small (solid curve) but the cyclic voltammogram of UA at $CaFe_2O_4$ NPs/CPE (dash curve) shows a significant enhancement of oxidation peak current at peak potential 0.29 V. Further the scan rate effect was done by varying the scan rate from 50 to 500 mVs^{-1}. Anodic peak current (IPa) of UA was increased with increased scan rate (Fig.4b).The graph of anodic peak current v/s scan rate shows linear relationship and correlation coefficient was found to be 0.9963 (insert Fig 4b). the concentration effect was done by varying the concentration from 3×10^{-4} to 13×10^{-4} M anodic peak current (IPa) of UA was increased with increased concentration (Fig.4c).The graph of anodic peak current v/s concentration of UA was shown good linearity and correlation coefficient was found to be 0.9915 (insert Fig 4c).
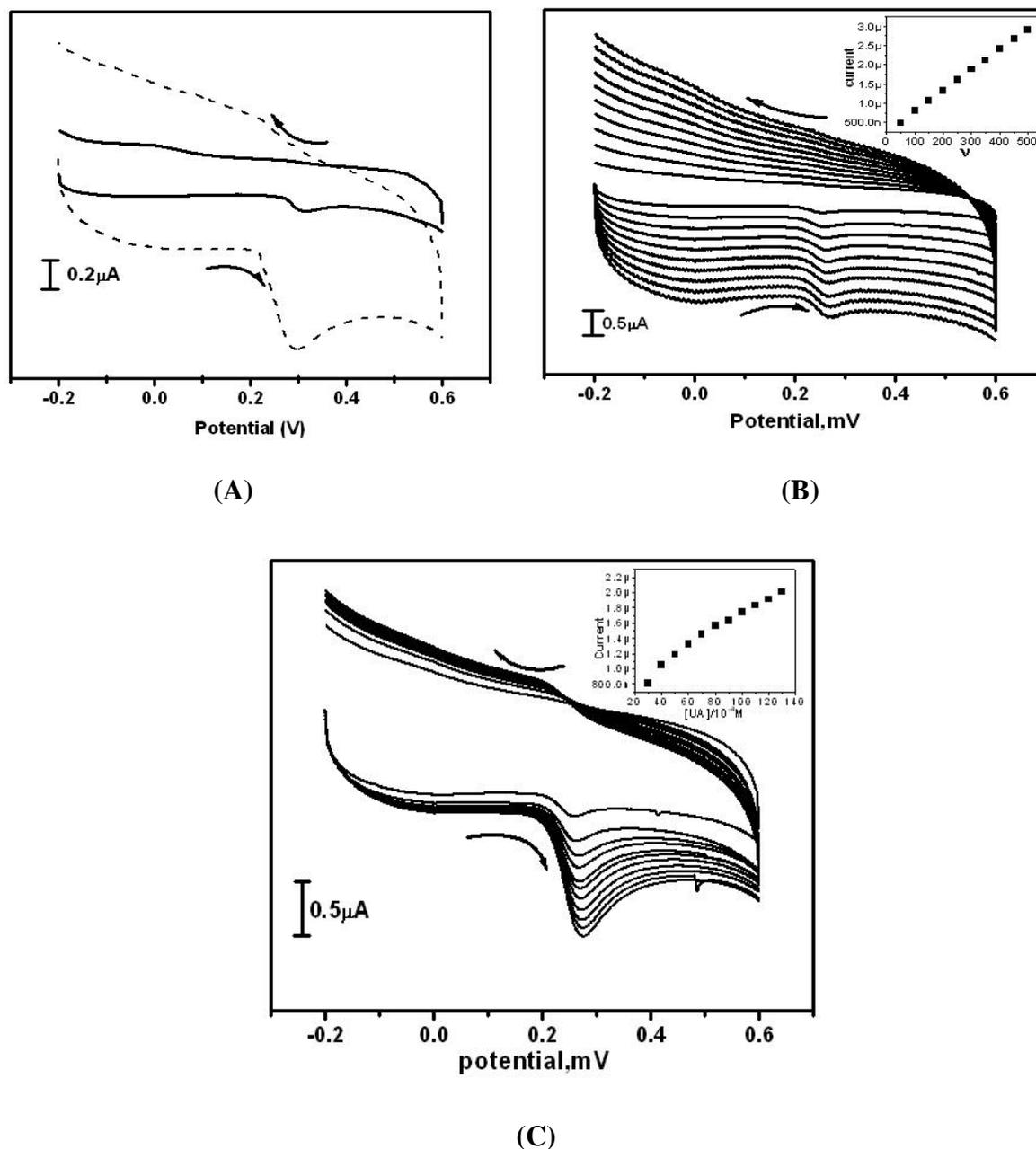
(A)

(B)

(C)

Fig. 4 (A). Cyclic voltammogram of 1×10^{-4} M UA in PBS at pH 7.4 at solid line for bare and dashed line for CaFe$_2$O$_4$ NPs MCPE; **(B)** Cyclic voltammograms of CaFe$_2$O$_4$ NPs MCPE in PBS solution pH 7.4 with different scan rate UA (50–500 mVs^{-1}). Inset shows the Graph of anodic peak current v/s scan rate of UA; **(C).** Cyclic voltammograms of CaFe$_2$O$_4$ NPs MCPE in PBS solution pH 7.4 with different concentration UA (0.3 to 0.13 μM). Inset shows the Graph of anodic peak current v/s concentration of UA

From the (Fig. 5a) peak current of FA at a bare carbon paste electrode was small (solid curve) at sweep rate 100 mVs^{-1} in 0.2 M phosphate buffer solution of pH 7.4. The obtained voltammogram at CaFe$_2$O$_4$ Nps/CPE for FA (dash line) shows a significant enhancement of oxidation peak current at peak potential 0.68 V. The scan rate study was done by varying the

scan rate from 50 to 500 mV/s^{-1}. The anodic peak current was increased with increase in the scan rate (Fig 5b). The graph of anodic peak current v/s scan rate results in linear relationship and correlation coefficient was found to be 0.99676 (insert Fig.5b). the concentration effect was done by varying the concentration from 2×10^{-4} to 11×10^{-4} M the anodic peak current (IPa) of FA was increased with increased concentration (Fig 5c) The graph of anodic peak current v/s concentration of FA was shown good linearity and correlation coefficient was found to be 0.9967 (insert Fig 5c).
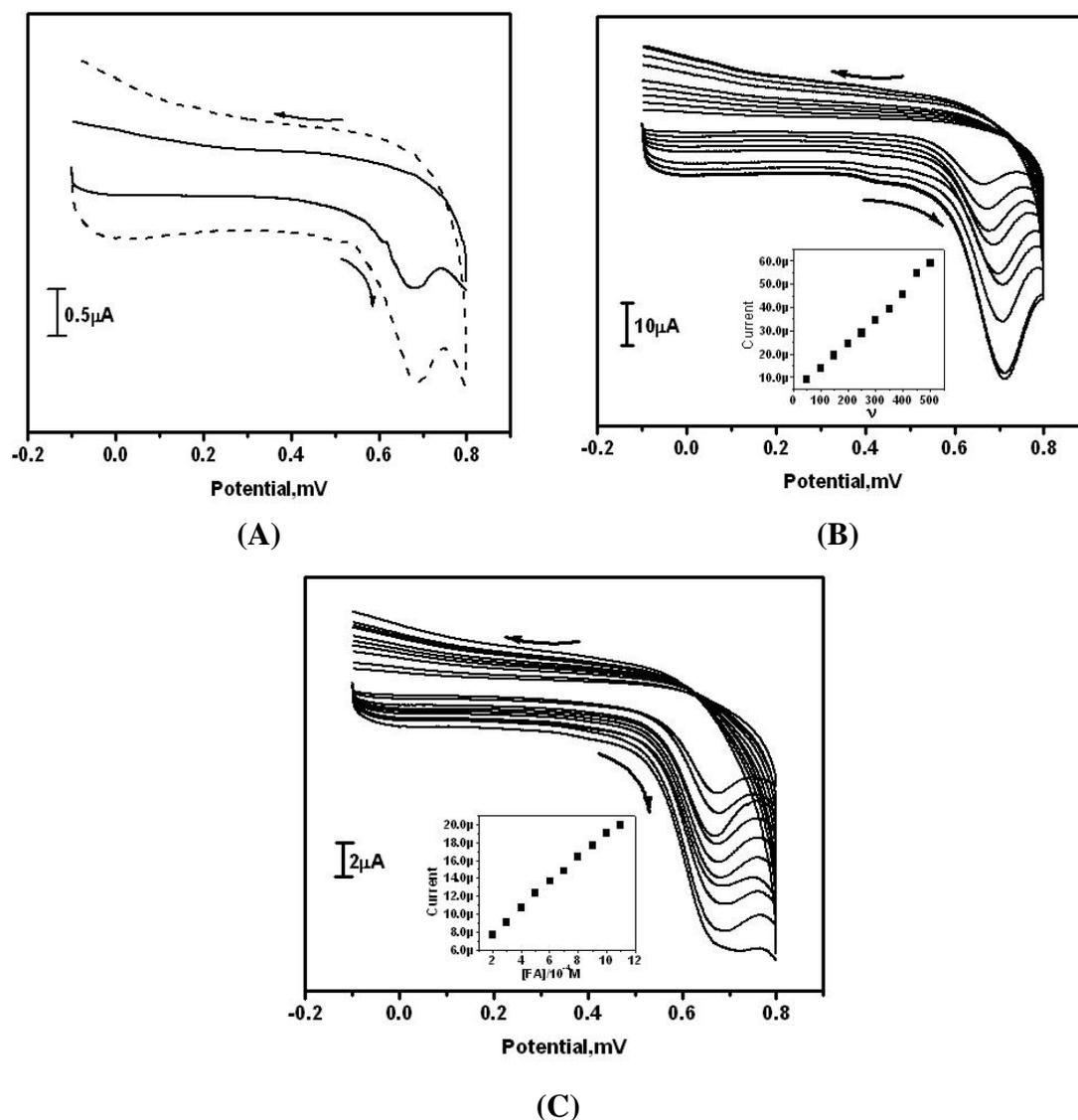

(A)

(B)

(C)

Fig. 5 (A). Cyclic voltammogram of 1×10^{-4} M FA in PBS at pH 7.4 at solid line for bare and dashed line for CaFe$_2$O$_4$ NPs MCPE; **(B).** Cyclic voltammograms of CaFe$_2$O$_4$ NPs MCPE in PBS solution pH 7.4 with different scan rate FA (100 to 500 mVs^{-1}). Inset shows the Graph of anodic peak current v/s concentration of FA; **(C).** Cyclic voltammograms of CaFe$_2$O$_4$ NPs MCPE in PBS solution pH 7.4 with different concentration DA (0.2 to 0.11 μM). Inset shows the Graph of anodic peak current v/s concentration of FA

3.7. Simultaneous Determination of DA, UA and FA

The electrochemistry of these three components at bare CPE (dashed line) and a $CaFe_2O_4$ Nps/CPE (solid line) in 0.2 M PBS (pH 7.4) containing mixture of 1×10^{-4} M DA, 3×10^{-4} M UA and 2×10^{-4} M FA was studied by CV technique. On the blank CPE the electrochemical responses of the mixture solution does not showed any peak and modified with $CaFe_2O_4$ NPs CPE, the electrochemistry responses of the mixture solution clearly showed three well resolved anodic peak at 0.13 V, 0.31 V and 0.68 V respectively for the electrooxidation of DA, UA and FA which is good enough to determine these species in their mixtures it showed in Fig 6.
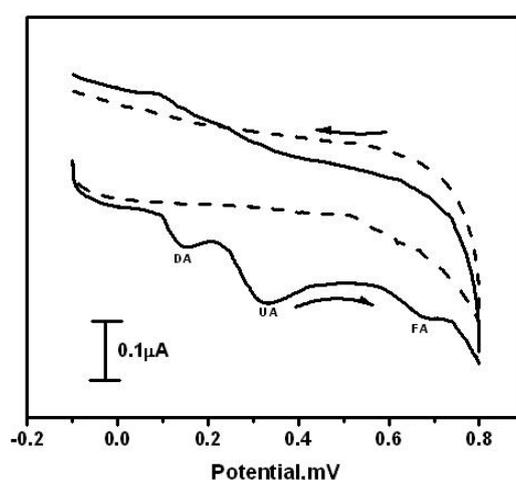

Fig. 6. Cyclic voltammograms of 1×10^{-4} M DA, 2×10^{-4} M UA and 3×10^{-4} M FA in their mixture $CaFe_2O_4$ NPs MCPE (solid line) and blank (dashed line) in PBS at pH 7.4

4. CONCLUSION

The present study $CaFe_2O_4$ NPs was synthesized by solution based method with average crystalline size 62 nm and their electrochemical parameters where study. The $CaFe_2O_4$ NPs where used as a modifier for the CPE and for the detection of DA in presence of phosphate buffer solution pH 7.4 at a scan rate of 100 mVs^{-1} in both CV and DPV techniques. From the scan rate study the electrode process was controlled by both adsorption and diffusion process occurring at the $CaFe_2O_4$ NPs modified CPE and the detection limit was found to be 1×10^{-4} M. From the comparative study of BCPE and $CaFe_2O_4$ NPs modified CPE. The modified CPE shows good electrochemical sensitivity to words the DA, UA and FA. From their results, we concluded that the MCPE had good electrocatalytic activity and it could hold the great application in the field of biosensors.

REFERENCES

[1] V. Sepelak, and K. D. Becker, Mater. Sci. Eng. A 375–377 (2004) 861.

[2] V. Sepelak, I. Bergmann, A. Feldhoff, P. Heitjans, F. Krumeich, D. Menzel, F. J. Litterst, S. J. Campbell, and K. D. Becker, J. Phys. Chem. C 111 (2007) 5026.

[3] N. Sivakumar, A. Narayanasamy, N. Ponpandian, and G. Govindaraj, J. Appl. Phys. 101 (2007) 84116.

[4] V. V. Boldyrev, Russ. Chem. Rev. 75 (2006) 177.

[5] N. Ikenaga, Y. Ohgaito, and T. Suzuki, Energy Fuels 19 (2005) 170.

[6] D. Hirabayashi, Y. Sakai, T. Yoshikawa, K. Mochizuki, Y. Kojima, K. Suzuki, K. Ohshita, and Y. Watanabe, Hyper. Inter. 167 (2006) 809.

[7] E. V. Tsipis, Y. V. Pivak, J. C. Waerenborgh, V. A. Kolotygin, A. P. Viskup, and V. V. Kharton, Solid State Ionic. 178 (2007) 1428.

[8] S. B Hana, F. F. Abdel-Mohsen, and H. S. Emira, Interceram 54 (2005) 106.

[9] N. Sharma, K. M. Shaju, G. V. Subba Rao, and B. V. R. Chowdari, J. Power Sou. 124 (2003) 204.

[10] D. Hirabayashi, T. Yoshikawa, K. Mochizuki, K. Suzuki, and Y. Sakai, Catal Lett. 110 (2006) 269.

[11] R. A. Candeia, M. I. B. Bernardi, E. Longo, I. M. G. Santos, and A. G. Souza, Mater. Lett. 58 (2004) 569.

[12] X. Ma, M. Zheng, W. Liu, Y. Qian, B. Zhang, and W. Liu, J. Hazard. Mater. 127 (2005) 156.

[13] V. Berbenni, A. Marini, G. Bruni, and C. Milanese, J. Anal. Appl. Pyrol. 82 (2008) 255.

[14] L. A. Isupova, S. V. Tsibulya, G. N. Kryukova, A. A. Budneva, E. A. Pau-kshtis, G. S. Litvak, V. P. Ivanov, V. N. Kolomiichuk, Y. T. Pavlyukhin, and V. A. Sadykov, Kinet Catal. 43 (2002) 122.

[15] M. I. Gomez, J. A. de Moran, R. E. Carbonio, and P. J. Aymonino, J. Solid State Chem. 142 (1999) 138.

[16] L. J. Berchmans, M. Myndyk, K. L. Da Silva, A. Feldhoff, J. Subrt, P. Heitjans, K. D. Becker, and V. Sepelak, J. Alloy. Compd. 500 (2010) 68.

[17] A. Sawa, and S. H. Snyder, Science 296 (2002) 692.

[18] G. A. Junter, Electrochemical Detection Techniques in the Applied Biosciences, Halsted, New York (1988).

[19] Q. Wang, D. Dong, and N.Q. Li, Bioelectrochemistry 54 (2001) 169.

[20] K. H. Xue, F. F. Tao, and W. Xu, J. Electroanal. Chem. 578 (2005) 323.

[21] M. Chicharroa, A. Sancheza, A. Zapardiel, M. D. Rubianesc, and G. Rivasc, Anal. Chim. Acta 523 (2004) 185.

[22] L. Yavich, and J. Tiihonen, J. Neurosci. Method. 104 (2000) 55.

[23] F. Arslan, Sensors 8 (2008) 5492.

[24] J. M. Zen, and J. S. Tang, Anal. Chem. 67 (1995) 1892.

[25] M. H. Alderman. Curr. Opin. Pharm. 2 (2002) 126.

[26] J. S. Rodman, J. J. Williams, and C. M. Peterson, J. Urology 131 (1984) 1039.

[27] C. R. Raj, and T. Ohsaka, J. Electroanal. Chem. 540 (2003) 69.

[28] S. A. Wring, and J. P. Hart, Analyst 117 (1992) 1215.

[29] O. Gilbert, U. Chandra, B. E. K. Swamy, M. Panduranga Char, C. Nagaraj, and B. S. Sherigara, Int. J. Electrochem. Sci. 3 (2008) 1186.

[30] A. L. Lehninger, Principles of Biochemistry, Worth, New York (1982).

[31] G. R. Rao, G. Kanjilal, and K. R. Mohan, Analyst 103 (1978) 993.

[32] M. W. Dong, J. Lepore, and T. Tarumoto, J. Chromatogr. 442 (1988) 81.

[33] C. Paveenbampen, D. Lamontanaro, J. Moody, J. Zaremo, and C. J. Rehm, J. Pharm. Sci. 75 (1986) 1192.

[34] O. Gilbert, B. E. K. Swamy, U. Chandra, and B. S. Sherigara, Int. J. Electrochem. Sci. 4 (2009) 582.

[35] M. Pandurangachar, B. E. K. Swamy, B. N. Chandrashekar, O. Gilbert, S. Reddy, and B. S. Sherigara, Int. J. Electrochem. Sci. 5 (2010) 1187.

[36] S. Rekha, B. E. K. Swamy, R. D. V. Krishna, O. Gilbert, U. Chandraand, and B. S. Sherigara, Int. J. Electrochem. Sci. 4 (2009) 832.

[37] S. Reddy, B. E. Kumara Swamy, U. Chandra, B. S. Sherigara and H. Jayadevappa, Int. J. Electrochem. Sci. 5 (2010) 10.

[38] U. Chandra, B. E. Kumara Swamy, O. Gilbert, M. Pandurangachar, S. Reddy, S. S. Shankar, and B. S. Sherigara, Chin. Chem. Lett. 21 (2010) 1490.

[39]   G. Wang, J. Sun, and W. Zhang, Microchim. Acta 164 (2009) 357.

[40] U. Chandra, B. E. K. Swamy, O. Gilbert, and B. S. Sherigara, Anal. Method. 3 (2011) 2068.

[41] R. N. Goyal, A. Aliumar, and M. Oyama, J. Electroanal. Chem. 58 (2009) 631.

[42] S. Reddy, B. E. Kumara Swamy, Umesh Chandra, K. R. Mahathesha, T. V. Sathisha, and H. Jayadevappa Anal. Method. 3 (2011) 2792.