Int. J. Electrochem. Sci., 12 **(2017)** 1572 – 1588, doi: 10.20964/2017.02.76

International Journal of
ELECTROCHEMICAL
SCIENCE
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Review

Recent Progress and Perspective Design of Various Electrode Catalysts for the Simultaneous Determinations of Dopamine in the Presence of Ascorbic Acid and Uric Acid: A Review

Rasu Ramachandran[1], *Tse-Wei Chen*[2,6], *Shen-Ming Chen*[2,*], *George peter Gnana kumar*[3], *Muthiah Chinnasamy*[4], *Natrajan Biruntha Devi*[5] , *Tien-Wen Tseng*[6]

[1]Department of Chemistry, The Madura College, Vidya Nagar, Madurai - 625 011, Tamil Nadu, India.
[2]Electroanalysis and Bioelectrochemistry Lab, Department of Chemical Engineering and Biotechnology, National Taipei University of Technology, No.1, Section 3, Chung-Hsiao East Road, Taipei 106.Taiwan (ROC).
[3]Department of Physical Chemistry, School of Chemistry, Madurai Kamaraj University, Madurai - 625 021, Tamil Nadu, India.
[4]Department of Inorganic Chemistry, School of Chemistry, Madurai Kamaraj University, Madurai - 625 021, Tamil Nadu, India.
[5]Department of Chemsitry, S.Vellaichamy Nadar College, Nagamalai pudukkottai, Madurai - 625021, Tamil Nadu, India.
[6]Department of Chemical Engineering and Biotechnology, National Taipei University of Technology, No.1, Section 3, Chung-Hsiao East Road, Taipei 106.Taiwan (ROC).
[*]E-mail: smchen78@ms15.hinet.net

Received: 24 November 2016 / *Accepted:* 23 December 2016 / *Published:* 30 December 2016

The flexible electrochemical based biosensors have been fabricated by various suggested methods and the designed composite offer new possibilities for the evaluation of biosensor applications. The resulting composite brought new kind of capabilities, which were employed electrochemical performance and greatly enhanced electrocatalytic activities of DA, AA and UA. The reviewed electrode catalysts have extensively been used improved the electrocatalytic activity and quantitative estimation of real sample analysis from human urine and blood serum. We have briefly discussed different parameters on the basis of biosensors, such as sensitivity, selectivity, reproducibility, real sample analysis and electrode stability. This article offers useful way, which could expand low-cost electrode (disposable electrode) materials and hold great promise electrochemical biosensing devices for biosensor applications.

Keywords: Electrode catalysts, Biosensors, Dopamine, Ascorbic acid, Uric acid, Real sample, Electrode stability.

1. INTRODUCTION

Electrode materials have contributed significantly to developing electroanalytical solicitations in various fields. It delivers a multipurpose approach for the synthesis and enlargement of nano based electrode materials appropriate for applying in simultaneous determinations of dopamine (DA), ascorbic acid (AA) and uric acid (UA). Highly ordered amorphous carbon nitrite (a-CN_x) film electrode deposited on a stainless steel electrode by DC magnetron sputtering method. The amorphous structure and remarkable advantages of a-CN_x for electrochemical bio-sensing applications have been recognized so for [1]. Thermal deposition method was also used to fabricate graphene decorated with gold nanoparticles and β-cyclodextrine (AuNPs-β-CD-Gra) composite, but the composite showed excellent electro oxidation of biomolecules [2]. Polymerized film of acid chrome blue K (ACBK) can be deposited on GCE through electrodeposition method, they can be directly deposited on GCE, ACBK were still widely used in electrochemical biosensor analysis [3]. Mukdaisai *et al* [4] explored a novel and simple electrochemical method, which can be effectively and selectively for the determination of AA and UA by a palladium supported porous graphitized carbon monolith modified carbon paste electrode (PdNPs/CM/CPE). Interestingly, a disposable and sensitive screen-printed graphene electrode (SPGNE) influenced wide potential window, low background current and faster electron transfer reaction. The developed electrode revealed that, three well defined sharp anodic peak currents were obtained [5]. Prior to the focus on, poly(tyrosine)/carboxyl functionalized multi-walled carbon nanotube composite was extensively used for the analysis of AA, DA and UA, the observable oxidation potential differences of 160 and 150 mV (AA-DA and DA-UA), respectively [6]. Ye *et al* [7] during the electrochemical treatment of carboxylated graphene oxide to grow on lanthanum and glassy carbon electrode (GO-COOLa/GCE). Upon the modified electrode, which were affected by several factors, such as the effect of pH, scan rates and concentrations, respectively. Regarding, a chemically modified ZnCrFeO4 into multi-walled carbon nanotube paste (MWCNTs/$ZnCrFeO_4$/CPE) composite have been keen to the investigations of AA, acetaminophen (AC) and codine (CO) oxidation [8]. On an Evan blue polymer film modified glassy carbon electrode, dopamine oxidation peak occurred at around 182 mV. The simple and easily appreciable separation of the oxidation peak potential for DA-AA and DA-UA were exhibited about 182 and 180 mV [9]. Medeiros et al [10] reported that the fabrications amorphous carbon nitrite (a-CN_x) electrode was deposited on boron-doped diamond (BDD) electrode for the study of electrooxidation of DA and AA. Niu and his co-workers [11] objectively investigate the most successful nano-Au/DNA/nano-Au/poly(SFR)/GCE composite and promising approach for the detection of DA in the presence of AA, adenine (A) and guanine (G). Yue *et al* [12] demonstrated a novel experimental approach for the preparation of edge-plane-like defects, large surface area mesoporous structure of carbon nanofiber-modified graphite (MNCF/PGE) composite. They investigated the oxidation over the potential of biomolecules (DA, UA and AA) significantly decreases and dramatically increased their anodic peak currents. Poly(3,4-ethylenedioxythiophene-co-(5-amino-2-naphthalinesulfonic acid)) (PEDOT-PANS) modified polymer composite have great potential applications in biosensors for selective determinations of dopamine in the presence of AA and UA [13]. Rubianes *et al* [14] reported that carbon nanotube based melanic polymer (CNTPE) composite for highly sensitive and selective quantifications of dopamine. The employed dopamine detection limits have been estimated through both amperometry and adsorptive stripping method.

In this article, we represented abundant electrode materials and possible facile modifications of the suggested electrode catalysts to improve the simultaneous determinations of DA, AA and UA. Meanwhile, we highlighted the extensive research work in progress increase the electrode surface area and extensive electroanalytical techniques (Amperometry, DPV and SWV) for the analysis of bio-sensing molecules. So far, different parameters relevant to sensors have been discussed such as sensitivity, selectivity, reproducibility, real sample analysis and long term durability, respectively.

2. ELECTRODE CATALYSTS

2.1. Carbon electrode

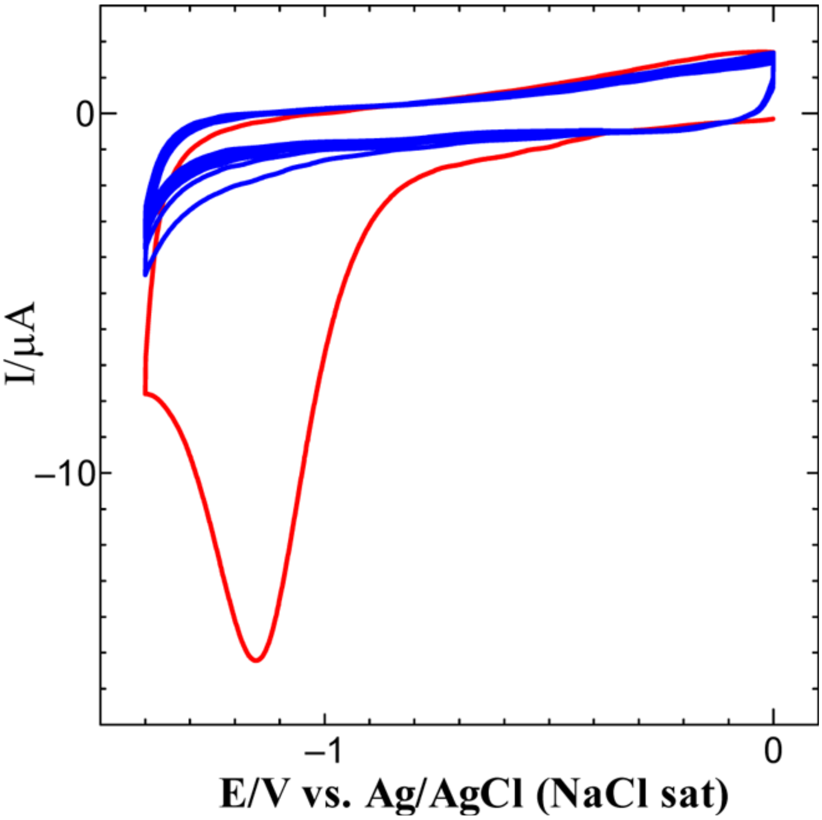

Figure 1. Electrochemical reduction of electrostatically assembled GO on GC/HDA electrode (15 cycles) in 0.2 M PB solution (pH 7.2) at a scan rate of 100 mV s^{-1}. ("Reprinted with permission from (*J. Phys. Chem. C 117 (2013) 4326-4335*). Copyright (2016) American Chemical Society")

Recently, carbon based electrode materials have been widely used in all kinds of electrochemical applications, such as energy storage devices, electrochemical sensors, enzymatic and non-enzymatic biosensors *etc*., It exhibits different morphological structures like fibers, wire, tubes and spherical. Mesoporous nitrogen based carbon (MNC) containing electrode has received much attention for examining superior electro sensitivity towards the oxidation of AA, DA and UA with their LOD of 0.01 μM, 0.001 μM and 0.01 μM [15]. The use of one dimensional (1D) carbon nanomaterials for the simultaneous determinations of DA, UA and AA. The geometrical structure of MWCNT exhibit high sensitivity and outstanding affinity of biosensors [16]. Atta *et al* [17] have used nano-perovskite carbon paste (CpE/$SrPdO_3$) composite electrode explored extensively for electrochemical sensing of dopamine in biological fluids. Thus, the electrode catalysts elucidate the oxygen-surface interaction between the oxygen atom of the hydroxyl groups and the transition of the Perovski element. Kiran *et al* [18] used a boron doped diamond (BDD) microelectrode; it reveals superior properties like low background current, low adsorption species, anti-fouling capabilities and long term stabilities for the quantification of uric acid in urine sample. Raj and his co-workers [19] investigated the electrochemical sensing of AA, DA and UA by using a novel electrochemical reduced graphene oxide (ERGO) film electrode. The self-assembled ERGO electrode has been prepared by electrochemically, the applied cycle between 0 to -1.4 V *vs* SCE for 15 cycles (Fig.1). A new type of N-doped functionalized MWCNT modified with Fe_3O_4 nanoparticle (Fe_3O_4@CNT-N) also widely used in the study of electrocatalytic activity, they functionalized Fe_3O_4@CNT-N composite has been used as a promising candidate for the simultaneous determinations of biosensors [20].

2.2. Metal oxide

The development of one dimensional (1D) magnesium oxide (MgO) nanostructure (Nanorod and nanobelt) based electrode catalysts were synthesized by plasma jet chemical vapour deposition (CVD) method for their simultaneous determinations of highly sensitive and selective analytical applications of DA, AA and UA [21]. Ghanbari *et al* [22] suggested electrochemical deposition/fabrication rout of flower like morphological zinc oxide/polyaniline/reduced graphene oxide (ZnO/PANI/RGO) nanocomposite was characterized by field emission scanning electron miscroscopy (FE-SEM), XRD, Raman and FT-IR spectroscopies. The nanofiber ZnO/PANI/RGO composite exhibit their average diameter of about 100 nm, the high surface area and good conductivity of nanocomposite allows efficient oxidations of DA and UA. Dopamine and paracetamol have been studied by using copper and copper (I) oxide (Cu/CuO) modified electrode. In this electrode surface will offer higher electrochemical performance indicating a great material for analytical applications [23]. Among the available rout, Hummers method is one of the versatile one for the synthesis of graphite oxide, which is mainly modified with tin oxide (SnO_2). The modified graphene/SnO_2 composite, the oxidation peak of AA, DA and UA obtained at 120, 281 and 408 mV, respectively, and it can lower over potential, increase sensitivity and reaction rate [24]. The use of a novel biosensor (Vertically aligned ZnO nanowire arrays) electrode can offer promising electroactive materials were studied for the simultaneous determinations of UA, DA and AA. Fig.2. (a) Shows the schematic formation of ZnO NWA/Graphene Foam (GC) electrode for the detection of biosensors. Fig. 2 (b) shows, the scanning electron microscope (SEM) image of ZnO NWA/GF electrodes was robust, aligned and highly uniform [25]. A smooth nanofiber morphological structure of zinc oxide and copper oxide decorated polypyrrole (ZnO-CuO-PPy) nanocomposite has been successfully fabricated by electrochemical method. The composite exhibit relatively a smooth nanofiber surface with the diameter value of 100 nm and it was characterized through Raman spectroscopy (C=C backbone polymer stretching at 1590 cm^{-1} & ring stretching mode at 1367 cm^{-1}).

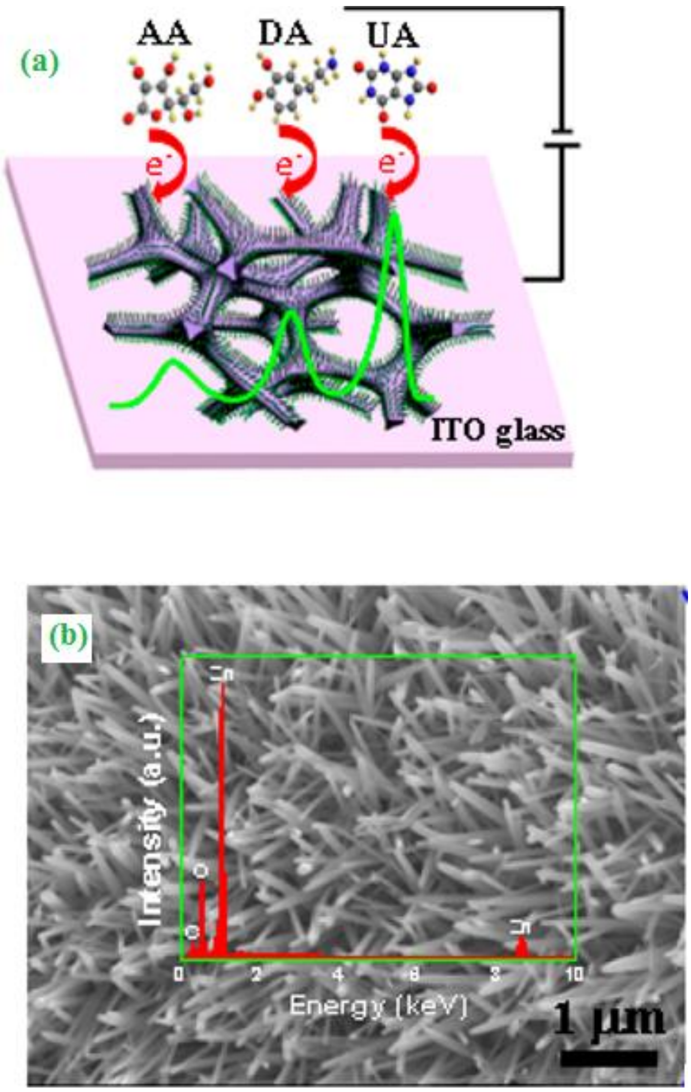

Figure 2. (a) Schematic of the ZnO NWA/GF electrode and detection of UA, DA, and AA. (b) SEM images of the ZnO NWAs on the 3D GF at different magnifications. Inset: EDX of the ZnO NWAs. ("Reprinted with permission from (*ACS Nano 8 (2014) 1639-1646*). Copyright (2014) American Chemical Society")

The proposed composite also applied for real sample of human urine analysis [26]. Wu *et al* [27] constructed a mesoporous structure and magnetic properties of amino functionalized ion oxide based graphene sheet (FeO3-NH2@GS) composite for the determinations of biomolecules (AA, DA and UA) because of their high sensitivity, simple operation and low expenses. Ruthenium oxide (RuO_2 xH_2O) has also been prepared by electrochemical deposition method under the optimized pH conditions in 2, the growth behaviour potential range between -0.2 to 1.05 V *vs* SCE. The electrochemical deposited RuO_2 was quantified through electrochemical quartz crystal microbalance (EQCM) and it can apply to simultaneous studies of bio molecules [28].

2.3. Conducting polymers

Conducting polymer exhibits great attention due to their widespread applications, such as high sensitivity, selectivity and lower background current. The advent of gold supported conducting polymer (Polyimidazole) based graphene oxide, which have been used in electrochemical research. Thus, the polymer nanocomposite (GNPs/PImox/GCE) has proven excellent electrocatalytic activities towards AA, DA, UA and tryptophan (Trp) [29]. The electrocatalytic active graphene/conducting polymer (Pol-4-amino-3-hydroxy-1-naphthalene sulfonic acid) nanocomposite has been prepared by electrochemical method. The electrode catalysts were successfully explored for simultaneous determination of dopamine and 5-hydroxytryptamine (5-HT) [30]. Interestingly, Prasad and his co-workers described the fabricated dual template imprinted polymer based MWCNT composite electrode surface considerable attention to a large electrode surface area and imprinted electrochemical properties.

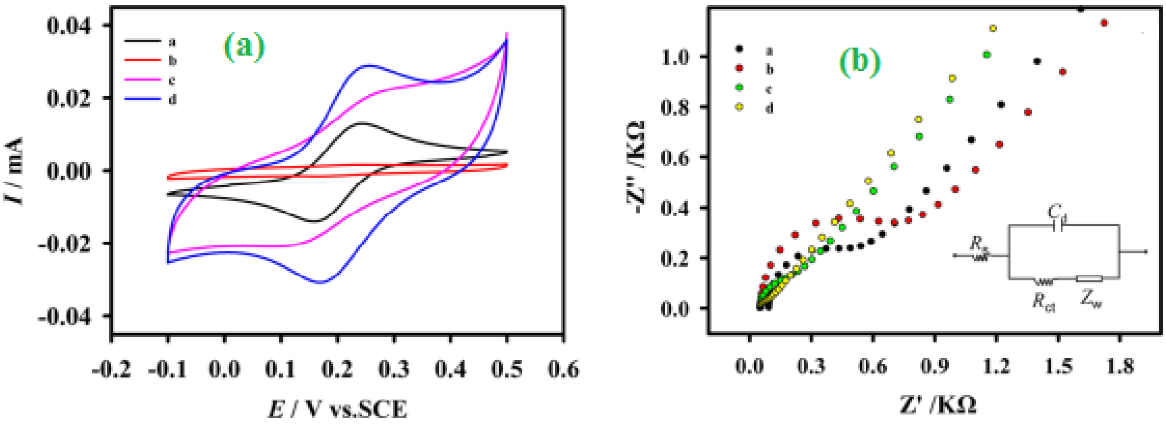

Figure 3. CVs (a) and EIS (b) of bare GCE (a), GO/GCE (b), PDA-rGO/GCE (c), and Fc-NH-PDA-rGO/GCE (d) in 2mM $Fe(CN)_6^{3-/4-}$ containing 0.1 M Na_2SO_4. ("Reprinted with permission from (*ACS Appl. Mater. Interfaces 7 (2015) 17935-17946*). Copyright (2015) American Chemical Society”)

The ability made high sensitivity and selectivity of AA and DA [31]. A simple, selective and cost-effective graphene coated by polydopamine on MWCNT (Pdop@GR/MWNT) nanocomposite was prepared by chemical method. The wrinkled type of morphologies has attracted unique optical, catalytic, mechanical, thermal and simultaneous determinations of electrochemical properties (DA and AA) [32]. Huang *et al* [33] used a highly sensitive rGO based self-assembled polydopamine (PDA-rGO) composite for the electrochemical analysis of DA, UA and hydroquinone. From Fig. 3(a) shows the cyclic voltammetry obtained at various electrodes (GCE, GO/GCE, PDA- rGO/GCE and Fc-NH-PDA-rGO/GCE) using 2mM ferrocyanide. On the other hand, the electron-transfer properties also characterized by electrochemical impedance spectroscopy (EIS) analysis (Fig. 3(b)). From Nyquist plot, PDA-rGO/GCE exhibited the diameter of the semi-circle region decreased to 110Ω, this is suggested that PDA-rGO displayed good conductivity and accelerate the speed of the electron-transfer reactions. Poly(tyrosine) based functionalized MWCNT composite could effectively modify the electron showed very much excellent characteristics in electrochemical sensors, better stability, more active site and reproducibility of AA, DA and UA [34]. Yang and co-workers obtained a facile synthesis of AuNPs@polyaniline (AuNPs@PANI) core-shell nanocomposite by used one step chemical oxidative polymerization of aniline. The core-shell of nanocomposites was exhibited excellent electrocatalytic activity in both neutral and alkaline media, the favourable over potential shift of DA and UA and dramatically increased their oxidation peak currents [35].

3. VARIOUS METHODS FOR FABRICATING ELECTRODE MATERIALS

Hummers method becomes popular one for the synthesis of graphene oxide from graphite powder, this reduced graphene further modified with zinc sulphide (ZnS) and cetyl trimethyl ammonium bromide (CTAB). The CTAB/rGO/ZnS composite employed in the biosensors, which were applied to the determinations of AA, DA and UA [36]. A tubular structure of mesoporous nitrogen rich carbon (MNC) materials has been synthesized through a template method. The tubular surface of the MNC working electrode with suitable electrode catalyst could be a solution obtained superior sensitivity towards the oxidation of AA, DA and UA in the lower range of sensing level [37]. Chemical method has been recognized as an efficient and versatile technique for the fabrication of graphitic carbon nitride nanosheet and graphene oxide (CNNS/GO) composite could improve the effect of layer-by-layer structure by π-π interaction. It can also developed distinguished sensitivity, selectivity and low level detection limits of AA, DA and UA [38]. Lan and Zhang [39] have used a simple and novel electrochemical methods for the polymerization of 6-thioguanine (6-TG) modified glassy carbon electrode (P6-TG/GCE). From the SEM investigation, the P6-TG/GCE film displayed homogeneous surface structure and irregular and continuous holes on the electrode surface for the electro oxidations of analysts. A highly oriented tube-like structure of graphene sheet and 3,4,9,10-perylenetetracarboxylic acid (GS-PTCA) electrodes were synthesized under sonication conditions via π-π stacking interaction. The method resulted in the formation of GS-PTCA exhibited like tube, crumpled and wrinkled structure etc., [40]. The other approaches involved in the preparation of silver nanoparticles supported modified carbon paste electrode (AgNPs/MCP) through a biological method under micro-wave assisted conditions. The prepared modified electrode has been characterized various analytical and electro analytical techniques and they were optimized pH for a suggested equal number of protons and electrons involved in the electro oxidation of dopamine [41]. Among them, carbon fibers/ZnO core-shell hybrid electrodes were synthesized by plasma-assisted method. The core-shell hybrids have drawn considerable attention, because they provide a portable and a green route for the construction of biosensor applications [42]. Polycetyltrimethylammonium bromide (Poly(CTAB)) nano rod possessing an average diameter of 100 nm and their average length of about 1.2 □m by electrochemical method. The nano rod based electrode catalyst can act as a promising platform for the construction of novel sensor [43]. Highly sensitive and selective biosensors of hierarchical nano porous gold-silver (HNP-AuAg) alloys were successfully prepared by a facile fabrication two-step dealloying method. Subsequently, HNP-AuAg alloy have been applied to construct excellent electrocatalytic activities towards the individual oxidations of dopamine (DA) and uric acid (UA) [44]. A hetero structure of graphene oxide nano ribbons modified core-shell multi-walled carbon nanotube (GONRs/MWCNT) electrode was prepared by microwave-assisted method. Fig. 4(a & b) shows the transmission electron microscopy of two different microwave power (150 and 250W) dependent tube-to-ribbon and nano ribbon morphological hetero structure of GONRs/MWCNT nanomaterials. The optimal microwave core-shell GONRs/MWCNT hetero structure resulted superior current enhancement and great degree of potential for novel bio-sensing platform [45].

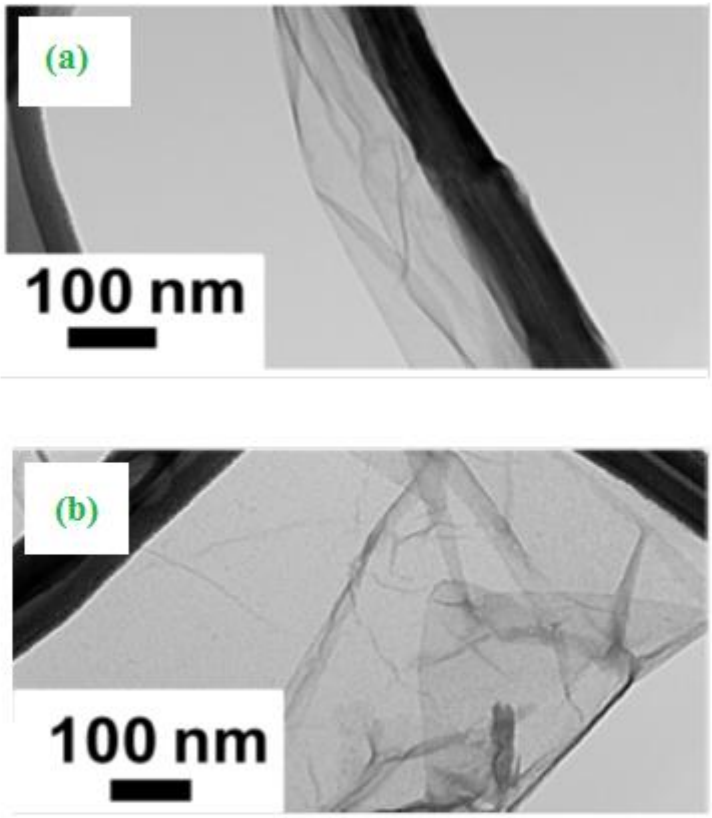

Figure 4. (a & b) Transmission electron microscopy images of a single as-received multi-walled carbon nanotube and graphene oxide nanoribbons derived from unzipping by treatment with $H_2SO_4 + H_3PO_4$ with dissolved $KMnO_4$ under microwave powers of 150 and 250 W applied for 4 min. ("Reprinted with permission from (*ACS Nano 5 (2011) 7788-7795*). Copyright (2011) American Chemical Society")

4. ELECTROANALYTICAL SENSITIVE TECHNIQUES

4.1. Amperometry

Amperometry is a powerful electrochemical tool for the analysis of electro active compounds like dopamine, uric acid, ascorbic acid, nitrobenzene, catecholamine and hydrazine at the range of nano molar to Pico molar level. In this type of electro analytical approach for the best suggested one of sensitivity, selectivity, simplicity of pre-treatment sample and stability of electrode modifications. Platinum nanosheet based fullerene (C_{60}) decorated on glassy carbon electrode (PtNSs/ C_{60}/GCE) through a simple potentiostatic deposition method. The as-prepared PtNSs/ C_{60}/GCE nanosheet composites were received excellent resolved peak potential (ΔE_{AA-DA} = 176 mV, ΔE_{DA-UA} = 132 mV and ΔE_{AA-UA} = 308 mV) values and stable electrocatalytic performance of AA, DA and UA [46]. On the other hand, there is a considerable interest in the development of vertically aligned RuO_2 based CNT modified (RuO_2/MWCNTs) electrode for the optimized sensor of dopamine. The displayed sensitivity (83.3 μA mM^{-1}) and detection limits (6.0 x 10^{-8} M) have been estimated through both DPV and amperometry [47].

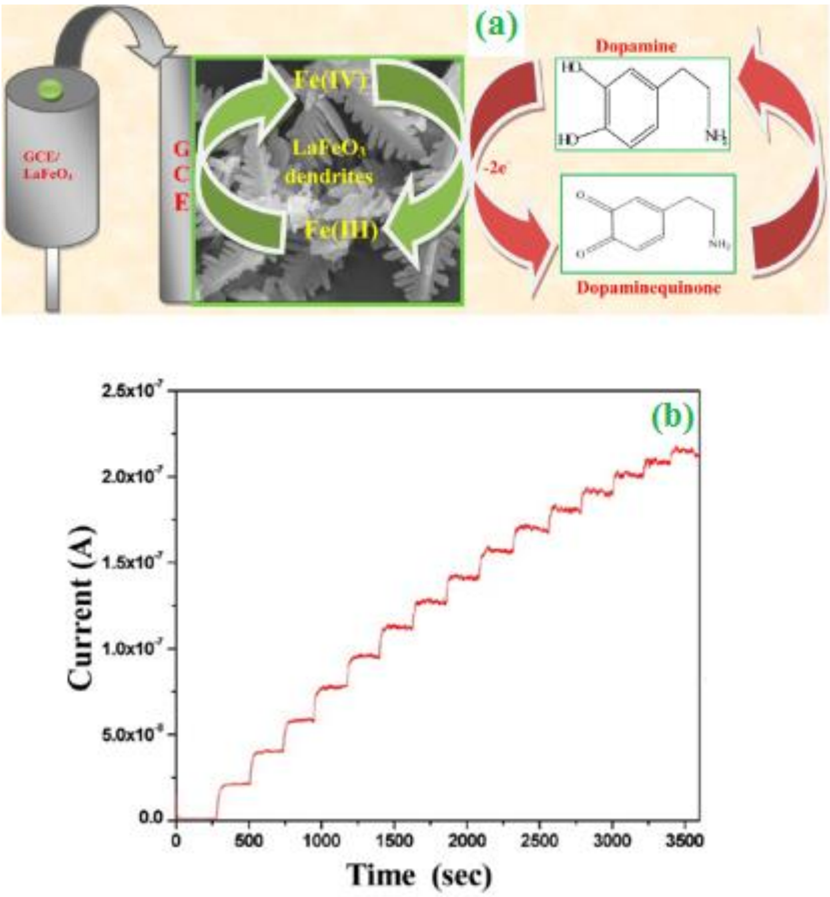

Figure 5. (a). Schematic illustration of electrocatalytic dopamine oxidation at the $LaFeO_3$ dendrite nanostructure modified GCE. **(b)** Amperometric i-t curve for the determination of DA at the $LaFeO_3$ dendrite modified electrode in 10 mM PBS 7.2. Each addition increases the concentration of 100 nM at regular intervals of 180s. ("Reprinted with permission from (*Cryst. Growth Des 13 (2013) 291-302*). Copyright (2013) American Chemical Society")

A novel carbon supported cobalt and nickel based nanomaterials play an important role in uric acid determinations and it was examined through amperometric method. The carbon supported nanomaterials demonstrated under neutral conditions, it may act as a cost effective, highly sensitive nature and long durable stability of the electrode surface [48]. Thakur *et al* [49] reported an amperometric biosensor based on platinum supported electrode, which can be modified with polyaniline-Prussian blue (PANI-PB) composite and it was displayed a satisfactory performance for the detection of uric acid. Moraes *et al* [50] used glassy carbon modified MWCNTs electrode doped with cobalt phthalocyanine (CoPc) by electrochemical method for the selective determinations of dopamine in the presence of ascorbic acid (LOD = 2.56 x 10^{-7} mol L^{-1}). A single crystalline sized and shape controlled novel $LaFeO_3$ dendric nano spheres have been synthesized by surfactant assisted hydrothermal processes (Fig. 5(a)). The $LaFeO_3$ dendrite modified electrode was performed the detection of dopamine analyte, the lowest limit of detection value of 62 nM (Fig. 5(b)) [51].

4.2. Differential pulse voltammetry (DPV)

In this technique is sensitive one, the following parameters are discussed such as pulse amplitude, pulse width and sample period. Recently, Ensafi and co-workers introduced a highly sensitive determination method for the simultaneous determinations of AA, DA and UA based on poly(sulfonazo III) modified glassy carbon electrode.

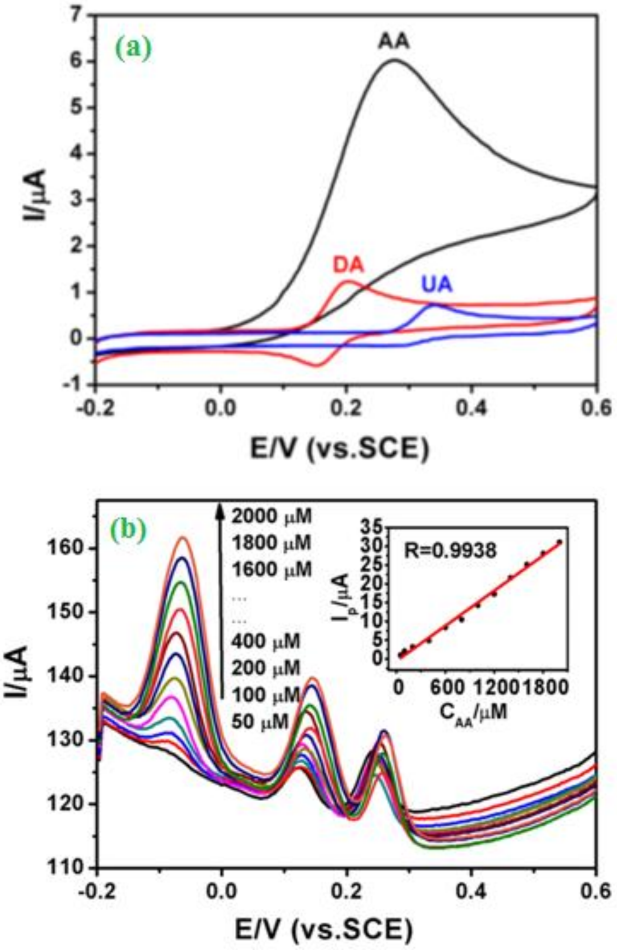

Figure 6. (a) Cyclic voltammetry's of 400 µM AA, 15 µM DA, and 30 µM UA at GCE **(b)** Differential pulse voltammetry at N-S-PC/GCE in 0.1 M PBS (pH 7.0) containing 3 µM DA, 4 µM UA, and different concentration of AA. ("Reprinted with permission from (*ACS Appl. Mater. Interfaces 6 (2014) 19109-19117*). Copyright (2014) American Chemical Society").

The results were achieved satisfactory one and for the real sample studies of Vitamin C tablets and Human sample [52]. However, the ultra-sized carbon supported Ni nanoparticles (Ni/C) has been prepared by chemical method (drop-coating). The Ni/C electrode reported remarkable increase of electron transfer kinetics of electroactive compound and significantly decrease in the over-potential for the oxidations of AA, DA and UA [53]. The advent a quite smooth three-dimensional morphology of electrochemically reduced graphene oxide modified carbon fiber (ErGO/CFE) electrode is a milestone in modern applied chemistry and they have been widely used as an electrocatalytic activity towards bio-sensing molecules. However, ErGO/CFE had three well defined peak potential values of 116, 167 and 283 mV for AA-DA, DA-UA and AA-UA respectively [54]. Functionalized flexible graphene nanofiber can be modified with $NiCoO_4$ nanowire (GF/ $NiCoO_4$) have proven to be an excellent transducer in biosensors, due to their unique morphology, enhanced electrochemical properties and more environment stability. The as-prepared GF/ $NiCoO_4$ fiber composite showed excellent promising perspective in biosensor applications [55]. Poly(*p*-xylenosulfonephthalein) film electrode has been deposited into an electrochemical sensor for biomolecules and strategies have included the electrochemical deposition (Applied potential value = -0.30 to +1.20 V *vs* SCE) method. The polymer based electrochemical sensor commonly used because of their very easy electrode fabrication, low cost and great utility for making a voltammetric sensor for the detection of AA, epinephrine (Ep) and UA [56]. Manjunatha *et al* [57] interested in the development of electrochemical sensing devices for use in easiness preparation of sodium dodecyl sulphate modified carbon nanotube electrode, excellent reproducibility, low-level detection limit and wide linear dynamic range. Zhang *et al* [58] focused a novel nano horn based carbon/poly(glycine) (CNHs) sensor, the active CNHs matrix possess excellent electrical conductivity and high electrode surface area. The electrochemical characterization of AA, DA and UA at various (GCE, porous carbon based PC/GCE, nitrogen-doped N-PC/GCE, dual-nitrogen and sulphur doped N-S-PC/GCE and without porous doped carbon (N-S-C/GCE)) electrodes have been investigated by cyclic voltammetry method (Fig. 6(a)). The insight of highly sensitive and their low level detection values were determined by differential pulse voltammetry as shown in Fig. 6(b) [59].

4.3. Square wave voltammetry (SWV)

It is an alternative sensitive technique, the improvement of sensitive cyclic voltammetry as an analytical tool is square wave voltammetry. Carbon paste modified with 1-butyl-4-methyl-pyridinium tetrafluoborate ionic liquid (BMPTB) has been successfully applied for the determinations of biomolecules, such as DA, AA and UA [60]. More recently, a novel strategy in Mn-SnO_2 (Mn-SnO_2/GCE) synthesis based on microwave irradiation method offers several advantages in pharmaceuticals and urine sample analysis. The synchronous changes of analyte linear response ranges between 5 – 500 μM (UA) and 1 – 500 μM (Folic acid) [61]. Moreover, by coupling with self-assemble method (Wet chemical method), the construction of cadmium telluride (CdTe) quantum dots (QD) can be achieved remarkable electrochemical biosensing (DA, AA and UA) applications [62]. A chemically (Fullenrene-C_{60}-modified gold) modified electrode possess a conductive electro active film for the linear calibration of biological (dopamine) molecules. The fullerene-C_{60}-coated gold electrode, which can be used as promoters for the enhancement of electron transfer rate and lowered the oxidation potential of DA [63].

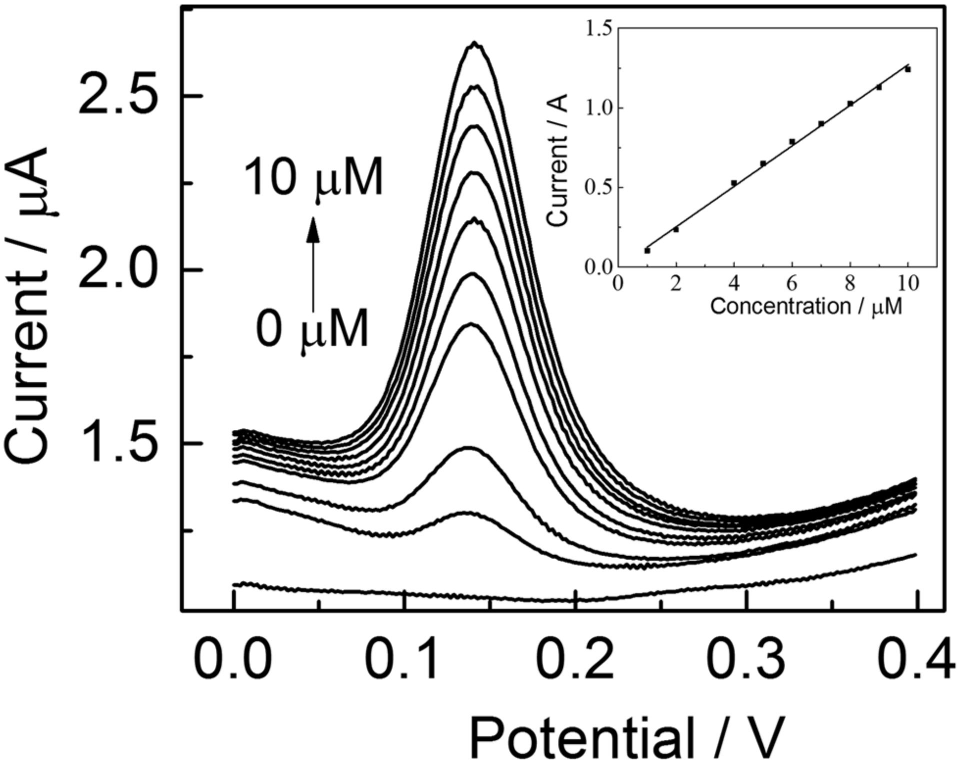

Figure 7. Square wave voltammetry in the potential range 0 to + 0.4 V at carbon-black modified glassy carbon (CB-GCE) in 0.1 M phosphate buffer with continual addition of dopamine (DA) such that [DA] varies between 0 µM to 10 µM. ("Reprinted with permission from (*ACS. Appl. Mater. Interfaces 8 (2016) 28338-28348*). Copyright (2016) American Chemical Society").

A simple, convenient and green rout of graphene decorated gold nanoparticle has been synthesized by *insitu* thermal reduction of graphene oxide and $HAuCl_2$ with β-Cyclodextrin (AnNPs-β-CD-Gra). The AnNPs-β-CD-Gra/GCE electrode was emerging as a possible strategy to improve linear response for AA, DA and UA and successfully applied for the determinations of UA in human urine [64]. The sono gel-carbon based modified L-Cystein electrode used as a new kind of electrode, which was exhibited excellent mechanical and electrical properties. It has also been used for the neat separation of two compounds with their peak-to-peak separations about 295 mV [65]. The cyclic voltammetry and square wave voltammetry were two main types of methods for the simultaneous analysis of AA, UA and DA by electrochemically reduced graphene oxide (GCE/RGO) electrode [66]. Beitollahi *et al* [67] have fabricated a novel CdTe quantum dot-modified carbon paste electrode (QDMCPE). The novel modified quantum dot electrode was examined as a simple, selective and new electrochemical determination of DA and UA in real samples. Jiang *et al* [68] explored the possibility and facile modifications of carbon-black based modified (CB-GCE) electrode to improve the detection of dopamine (Neurotransmitter) in the presence of AA and UA (Fig.7).

5. ELECTRODE STABILITY

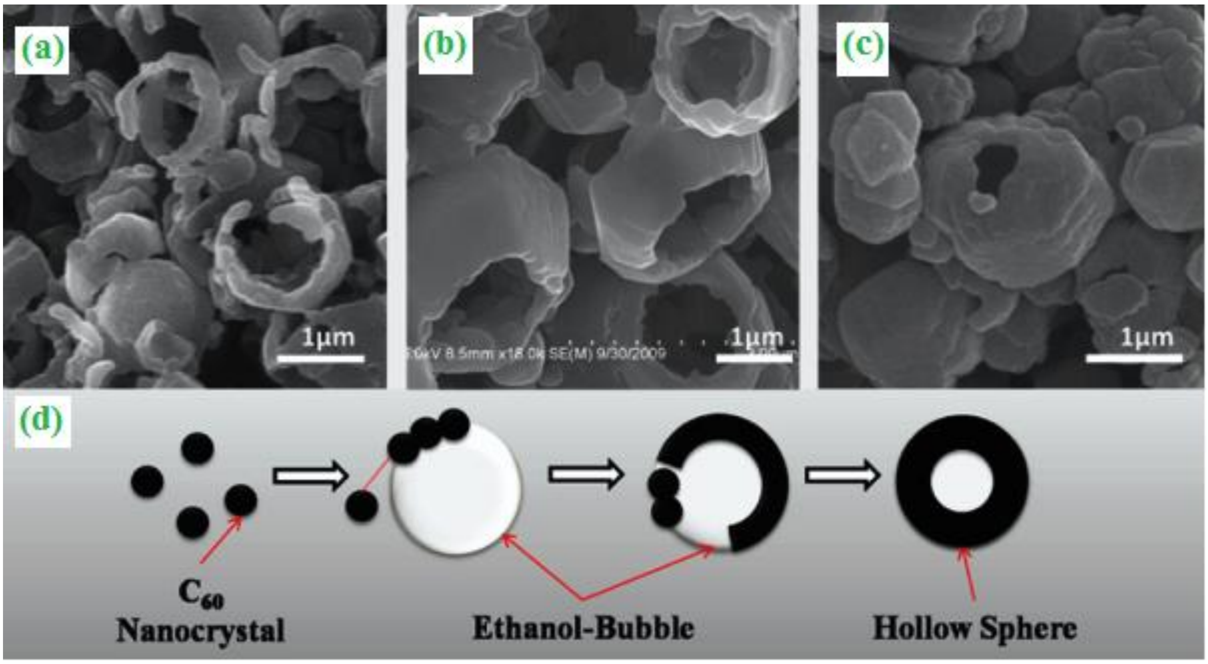

Figure 8. Studies on the plausible mechanism for the formation of C_{60} hollow microspheres. SEM of (a) C_{60} hemi-rings, (b) bows, and (c) almost completely spheres and (d) Plausible mechanism for the formation of C_{60} hollow microspheres with bubble-template. ("Reprinted with permission from (*ACS Appl. Mater. Interfaces 4 (2012) 1594-1600*). Copyright (2012) American Chemical Society").

The long-term durability of electrode catalyst is one of the most important parameters in practical studies of electrochemical applications. Mainly, the stability of different electrode catalysts was investigated through chronoamperometry method. Highly porous and hollow microspheres (Fig.8) SEM structures of C_{60} have been prepared by bubble-Template method. The hollow spheres C_{60}-modified electrode showed a high specific surface area (107 m^2 g^{-1}) and electrode stability of the re-used fullerene modified electrodes have been detected four biomolecules (DA, AA, UA and L-cysteine). [69]. A glassy carbon based poly(bromocresol green) electrode have found wide application in biosensor analysis. Commonly used uric acid, dopamine and ascorbic acid. The modified green electrode exhibited excellent electrocatalytic properties and their electrode storage maintained at 95.24 % (30 days) for good stability [70]. Most of the attention has been focused on the carboxylated single-walled carbon nanotube modified gold electrode surface for the investigations of the charge-transfer processes and kinetic studies used uric acid [71]. The nitrogen doped-MWCNTs possess high effective electrode surface area and it was further modified with metal nanoparticles (Pd, Ir, Pt and Au nanoparticles) (N-MWCNTs/MNPs) can be considered as a potential electrode materials for electrochemical analysis. The stability of the N-MWCNTs/MNPs composite tested systematically for about one week, after continuous usage for electrochemical analysis only 10-15 % decreased value of the initial response [72]. The recent developed chemical methods Azure-A mediated adsorption of colloidal gold nanoparticles was modified on the MWCNTs (Nafion/AuNPs/AzA/MWCNTs). The

Azur-A supported gold supported nanocomposites have drawn special research attention, because the composite attributed unique properties and possible electrochemical applications were carried out by both cyclic voltammetry and electrochemical impedance spectroscopic methods [73]. The carbon-ceramic electrode (CCE) was prepared by the sol-gel method. The simple and fast procedure MWCNTs were drop casted on the CCE. The chemically modified MWCNTs/CCE composite was employed biosensor applications and exhibited excellent electrocatalytic activities, reduced the oxidation over potential values and significantly increased oxidation of peak currents, respectively [74]. Moreover, there has been fabricated a new bio-sensors, a significant interest for the immobilization of quercetin in the modified silver nanoparticles and graphene nano sheets (Q-AgNPs-GNs-GCE). The quercetin immobilized AgNPs based composite attracted considerable interest in kinetics (Heterogeneous electron rate transfer processes "k") studies; voltammogram showed surface confined processes and employed high catalytic activity for L-Cysteine (L-Cys) oxidation [75].

6. REAL SAMPLE ANALYSIS

Zhu *et al* [76] have used a novel water-soluble multi-nano pore graphene modified glassy carbon (mp-GR) electrode by a hydrothermal method. However, the mp-GR/GCE exhibited abundant functional groups, edges and developed for the determinations of DA and UA in human real sample analysis. Great efforts have been used for the fabrication of graphene oxide nanoribbons (GONRs) modified with core-shell MWCNT taking advantages of the electrochemical analysis of AA, DA and UA. The core-shell hetero structure of MWCNT/GONR composite exhibited great degree of potential applications in biosensors platforms [77]. Also, the combinations of copper nanoparticles and poly(3-amino-5-mercapto-1,2,4-triazole) (P-TAox) film electrode not only could significantly improve the electrocatalytic properties and good bio-compatibility, flexibility and excellent electrode stability of the electrode materials. In order to confirm the applicability of the proposed CuNPs/P-TAox sensors were evaluated by the measurements of AA, DA, UA and Trp in human blood and urine sample [78]. Among them, gold and platinum supported poly(3,4-ethylenediaminethiophene) (Pt/PEDOT-Pt-Ag/AgCl and Au/PEDOT-Pt-Ag/AgCl) electrochemical microcell was one of the widely used conducting polymers for the detection of AA, DA, UA and exhibited high sensitivity, lower oxidation potential and low level detection limit. They addressed for the study of real sample of blood sera and urine of clinical diagnosis [79]. Li *et al* [80] have used a highly sensitive and selective of poly (Chromotrope 2B) (PCHAGCE) film electrode for the quantitative determinations of DA from human urine real sample. Uzun *et al* [81] have electrochemically prepared N,N'-bis(indole-3-carboxaldimine)-1,2-diaminocyclohexane (ICDACH) electrode for the determinations of DA by using the standard addition method in real sample.

7. CONCLUSIONS

In this article, flexible biosensors have been fabricated by various methods and biocatalysts for simultaneous determinations of dopamine in the presence of ascorbic acid and uric acid. Although, we have focused on advanced electrode materials (Carbon, metal oxide and conducting polymers) as novel catalysts for biosensor applications. The fabricated electrode catalysts have been studied under sensitive electroanalytical techniques (Amperometry, DPV and SWV). Here, the electrode catalysts would play an important role in the improvement of sensitivity, selectivity and lower level detection limits of three analytes (DA, AA and UA). Several important parameters also been discussed on the basis of biosensors, such as sensitivity, selectivity, reproducibility, real sample analysis and long term stability, etc., This article expanded and great promise for the scope of the applications in routine electrochemical sensing and biosensor analysis.

ACKNOWLEDGEMENT

We gratefully acknowledged, The Management and Chemistry Department Staff members, The Madura College, Madurai, Tamil Nadu, India.

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