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**Sensitive determination of acetaminophen in the presence of dopamine and pyridoxine
facilitated by their extent of interaction with single walled carbon nanotubes**

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Abstract

Single walled carbon nanotubes (SWCNTs) were immobilized on glassy carbon (GC) electrode by drop casting. The resulting modified electrode (represented as GC/SWCNTs) efficiently oxidizes acetaminophen (AC), dopamine (DA) and pyridoxine (PY) by decreasing the respective oxidation potentials and increasing peak currents in comparison to bare GC electrode. The extent of lowering overpotentials is in the order of AC > PY > DA, in agreement with the order of decrease in the HOMO-LUMO energy gap (ΔE) of these analytes, as determined from Density Functional Theory (DFT) calculations. DFT calculations further reveal that due to the adsorption of the analytes on the SWCNT(10,10) there is a negative charge density transfer (higher probability of electron transfer, lower ΔE value) to the frontier molecular orbitals of the analytes, which eases their oxidation. Since AC, DA and PY oxidize distinctly at distinct potential values, the present SWCNTs modified electrodes could be used to simultaneously determine them. Cyclic voltammetry, differential pulse voltammetry and amperometry techniques are utilized to understand the electrochemical characteristics of the analytes (AC, DA and PY) and subsequent sensing of them at the GC/SWCNTs electrode. The electrode is then applied to the determination of AC as a case study. Sensitivity, detection limit and linear calibration range for the AC are found to be $7.9 \mu\text{A } \mu\text{M}^{-1} \text{cm}^{-2}$, $1.1 \mu\text{M}$ and $2.0\text{-}100.0 \mu\text{M}$, respectively.

Keywords: Acetaminophen oxidation • Dopamine oxidation • Pyridoxine oxidation • Electrocatalysis • Single walled carbon nanotubes • DFT calculations

1 Introduction

Acetaminophen (AC) is a common antipyretic and analgesic drug which is mainly employed to decrease fever and to relieve pains associated with muscular, arthritis, post-operation, toothache, headache, backache, *etc.* [1-4]. In case of contraindication to aspirin, for instance, AC is considered as the best alternative for patients. Small dosages of AC generally do not cause any harmful side-effects; however over-dosage may lead to kidney and liver damages [3]. The long term use of AC may have fatal neurotoxic and hepatotoxic effects [2]. Thus, it is essential to get an accurate, easy to handle, fast and sensitive analytical technique for the frequent determination of AC [2]. Dopamine (DA) is a neurotransmitter which exists in central and peripheral nervous systems of mammals [1, 5, 6]. Low concentration levels of DA in human body generally lead to Parkinson's disease [1]. DA is supplied as medication to such patients, however excess dosage may cause increased heart beat and blood pressure because of its effect on sympathetic nervous system [1]. Therefore, regular monitoring of DA levels in human body is necessary [7]. Pyridoxine (PY), otherwise known as vitamin B₆ is a water soluble vitamin which plays significant role in body cells maintenance and in amino acids metabolism [8-10]. Three forms of PY are available which are known as, pyridoxal, pyridoxol and pyridoxamine [8-10]. PY is also necessary for physical and mental growth of the individual [11]. It is reported that vitamin B₆ imposes major effects on gene modulation, sexual behaviour, and immune modulation in HIV-1 infection [9]. Insufficient concentration level of PY in body leads to illness and various sicknesses such as hypertension, cardiovascular problems, hyperlipidemia, obesity and anaemia [8, 10, 11]. Hence, accurate PY determination is essential in human health diagnostics. Due to their complementary features/properties (nutrient, biologically important molecule, or drug), these compounds have been used as representative analytes in the context of the present study.

Variety of methods which include HPLC, flow injection analysis, liquid chromatography, *etc.* were reported for the sensing of the above analytes [1-18]. However, they can suffer from low selectivity, poor detection limit, tedious sample preparation procedure, high cost, *etc.* Electrochemical methods can offer several advantages like low detection limit, high high sensitivity and good selectivity if the electrode surface is modified with suitable catalytic materials. The electrode modification requires only small amount of additional materials and the resulting electrodes can decrease the electrode fouling effects and detect the target analytes at low overpotentials [19]. Recently, carbon based nanomaterials enticed the electrochemists extensively due to efficient promotion of electron transfer events on their surfaces [20-28]. Carbon nanotubes (CNTs) are attractive nanomaterials which possess several interesting properties from the electroanalytical point of view, including high conductivity, durable mechanical stability and high surface area [20-24]. These unique properties of CNTs are exploited in electrochemical science and technology to immobilize electrocatalysts and to increase the electrical communication within the immobilized molecules [20-24]. For example, increased oxidation currents are reported for cysteine, glucose, DA, epinephrine and ascorbic acid detection thanks to presence of CNTs on electrodes [22, 24, 29]. These huge improvements facilitated by the CNTs may be attributed to specific interactions of CNTs with the target analytes through π - π interaction and/or Van der Waals forces, or the presence of edge-plane-like defect sites [30-34]. In addition to these interactions, depending upon the functional groups of the analytes (phenolic, hydroxyl, amine and $-\text{NHCOCH}_3$ groups) they may have specific interactions to CNTs. Though numerous CNTs based composite materials are described to be beneficial in electrochemical sensing [20-24, 30-33], it should be noted here that the influence of CNTs alone on the electrochemical sensing process is not so studied in detail so far [1,17,29,35-38]. Hence, in

this study a simple, sensitive and cost effective electrochemical route for the efficient quantification of AC, DA and PY based on single walled CNTs immobilized glassy carbon electrodes is reported. The originality not only relies on the simultaneous analysis of these three analytes, but also on the use of additional theoretical calculations carried out to confirm the results obtained from electrochemical studies, which remains underexplored to date [39-41]. This work is expected to strengthen the existing knowledge on the adaptability of CNTs for the electroanalysis of biologically-relevant molecules.

2 Experimental

2.1 Reagents and chemicals

Single walled carbon nanotubes (SWCNTs), AC and DA were obtained from Sigma-Aldrich. Phosphate buffer of pH 7.0 (0.1 M) was prepared by mixing appropriate amounts of K_2HPO_4 and KH_2PO_4 (Qualigens, Mumbai, India) stock solutions. N, N-dimethyl formamide (DMF) and PY were purchased from S.D. Fine Chemicals, India. All chemicals were used as received and all solutions were prepared from triple distilled water.

2.2 Instrumental details

All electrochemical experiments have been performed using the CH Instruments' electrochemical workstation (model: CHI-660C), along with a three electrodes-single compartment cell system. Bare glassy carbon (GC) electrode or modified GC was used as working electrodes. A Pt wire and KCl saturated calomel electrode were employed as counter and reference electrodes, respectively. Electrochemical studies were carried out at room temperature in 0.1 M phosphate buffer (pH 7.0) unless otherwise mentioned. Prior to each electrochemical analysis, nitrogen gas was purged into the supporting electrolyte solution for 20 min to remove the dissolved oxygen.

2.3 Modification of working electrode

GC electrode was cleaned by rubbing it over the Buehler-felt pad with alumina slurry followed by ultra-sonication in triple distilled water. Colloid of SWCNTs was prepared in DMF (1.0%) by ultra-sonicating the mixture for 20 min. A 10 μL of the colloid was dropped over the clean GC electrode and dried for 12 h (represented as GC/SWCNTs).

2.4 Theoretical calculations

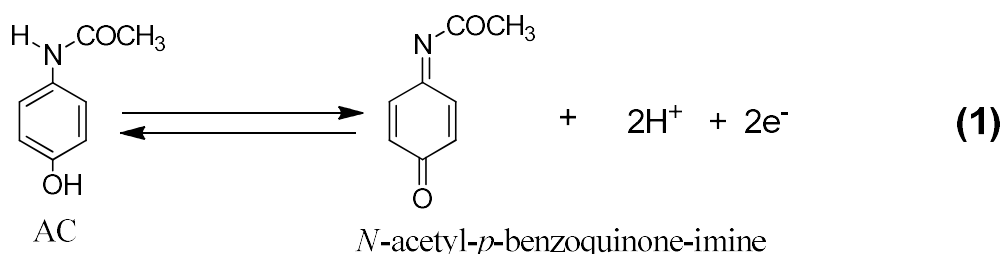
To understand the interaction between the SWCNTs and AC, DA and PY at the molecular level and hence to find out the change in oxidation properties of these molecules after adsorption onto SWCNTs, quantum chemical calculations were done based on the density functional theory (DFT, M06-2X/6-31G(d,p)). Gaussian 09 suits of program were used for the calculations [42]. For the SWCNT model, zigzag (10,10) nanotube was used (represented as SWCNT(10,10)). It contains five aromatic-ring chains and length of this SWCNT model can hold the target analytes (AC, DA and PY) well within the SWCNT structure.

3 Results and discussion

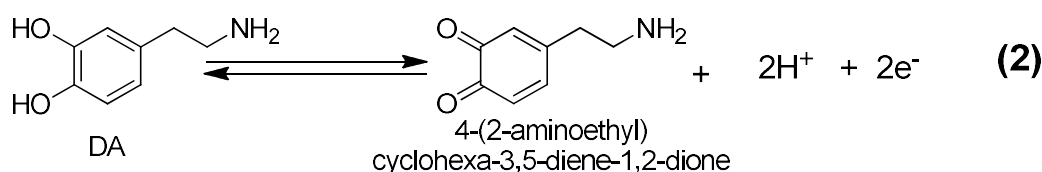
3.1 Cyclic voltammetry characterization of AC, DA, and PY at GC and GC/SWCNTs electrodes

Fig. 1 shows typical cyclic voltammograms (CV) recorded at a scan rate of 25 mV s^{-1} using GC and GC/SWCNTs electrodes for the oxidation of AC, DA, and PY in 0.1 M pH 7.0 phosphate buffer. CV responses clearly manifest the fact that both GC and GC/SWCNTs provide a potential window wide enough to examine the electrochemical behaviour of these

target analytes. The CV responses of 0.2 mM AC at bare GC and GC/SWCNTs electrodes are shown in Fig. 1a, corresponding to a well-established redox process (Eq. 1) [43]. Compared to the quasi-reversible signal for AC on bare GC electrode (with an anodic peak occurring at 510 mV), the use of GC/SWCNTs electrode results in lower overpotential for AC oxidation (anodic peak potential at 386 mV) and currents larger by more than one order of magnitude. The decrease in oxidation potential (124 mV) and huge increase in peak current (34 times) at GC/SWCNTs electrode indicate the efficient electrocatalytic effect exhibited by SWCNTs towards the oxidation of AC. During the reverse scan, it exhibits a reduction peak at 330 mV which may be ascribed as per the Eq. 1.



DA exhibits an oxidation peak around 245 mV at bare GC, while it shows a decreased oxidation peak potential (190 mV) with higher current at GC/SWCNTs (Fig. 1b), due to the oxidation of DA according to the process reminded at Eq. 2 [44]. The noticeable shift in the oxidation peak potential (55 mV) towards the less positive values with higher current (17 times) at GC/SWCNTs indicate confirm the electrocatalytic properties of SWCNTs towards DA oxidation [35]. The oxidized DA is reduced back in the reverse scan at 160 mV. The anodic to cathodic peak-to-peak separation of 30 mV is in good agreement with a fast electron transfer process.



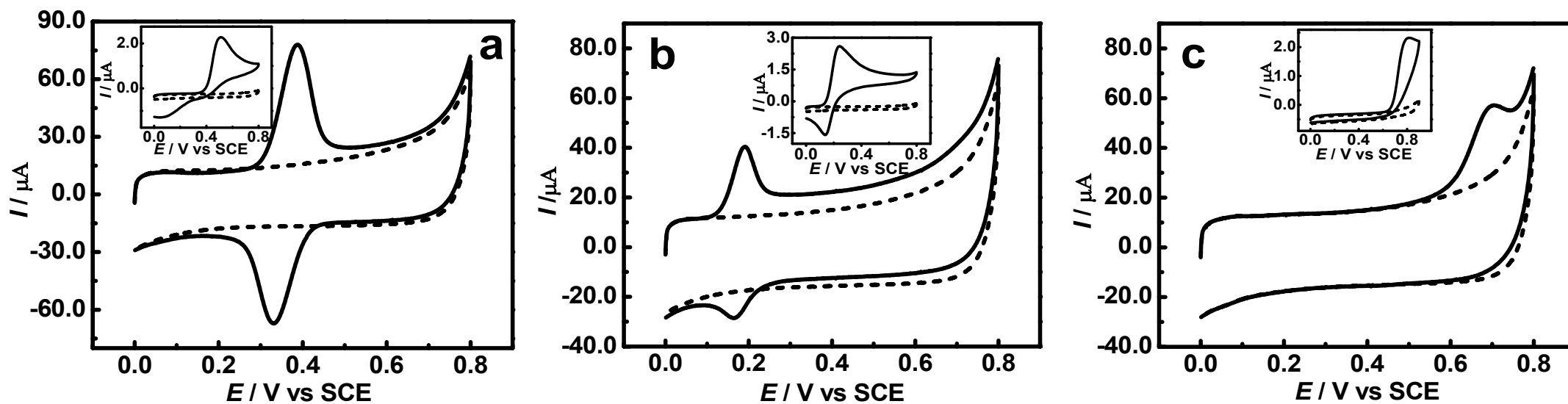
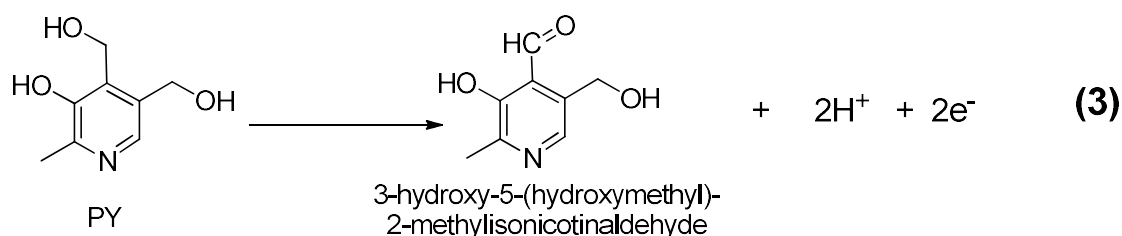


Fig. 1. CV curves recorded at GC/SWCNTs electrode in absence (*dashed line*) and presence (*solid line*) of 0.2 mM AC (a), 0.2 mM DA (b) and 0.2 mM PY (c) in 0.1 M pH 7.0 phosphate buffer (scan rate: 25 mVs^{-1}). Inset shows cyclic voltammograms recorded at bare GC electrode under the similar conditions.

Similarly, PY is oxidized at 812 mV with low current at bare GC, while easier oxidation takes place at GC/SWCNTs (peak potential around 700 mV, see Fig. 1c). The observed decrease in the oxidation peak potential (by 112 mV) with concomitant current increase (25 times) when passing from bare GC to the GC/SWCNTs demonstrate the catalytic properties of SWCNTs towards the oxidation of PY, although the overall process remains non reversible even at the GC/SWCNTs electrode. The probable reaction is shown in the Eq. 3 [8, 45].



From the above results, it is clear that all three analytes are oxidized electrocatalytically at the GC/SWCNTs electrode (based on the decrease in the oxidation overpotentials, and also the increase in oxidation currents but this latter has to be nuanced by the larger electroactive surface area provided by SWCNTs). The extent of decrease in oxidation peak potentials is found to be in the order of AC > PY > DA (130, 112, and 55 mV for AC, PY and DA, respectively).

DFT calculations are carried out to verify the conclusions drawn from CV experiments. Isosurfaces for the individual AC, DA and PY molecules as well as for their adsorption complexes with SWCNT(10,10) are shown (Fig. 2) to compare the changes in their electronic structure upon adsorption. From Fig. 2 one can see that the negative potential (shown in red) increases after adsorption of analyte molecules on the outer surface of SWCNT(10,10) when compared to the individual molecules, indicating that the oxidation potential decreases for all

the three compounds after adsorption, which is consistent with the above electrochemical observations. The extent of decrease in the oxidation potential might be correlated to the HOMO-LUMO energy gap ($\Delta E = E_{\text{LUMO}} - E_{\text{HOMO}}$) of the individual molecules. The lower is the ΔE value, stronger is the interaction with the SWCNT(10,10) due to the more facile electron transfer from the SWCNT(10,10) surface to the LUMO of the individual molecules. As a matter of fact that the removal of electron from the HOMO of the corresponding molecule (i.e., oxidation) will be easier and hence greater is the extent of the decrease in potential. The computed ΔE values for AC, PY and DA are 177.6, 180.8 and 185.1 kcal/mol, respectively. Therefore, the extent of decrease in oxidation potential would be in the following order: AC > PY > DA, which corroborates the experimental results.

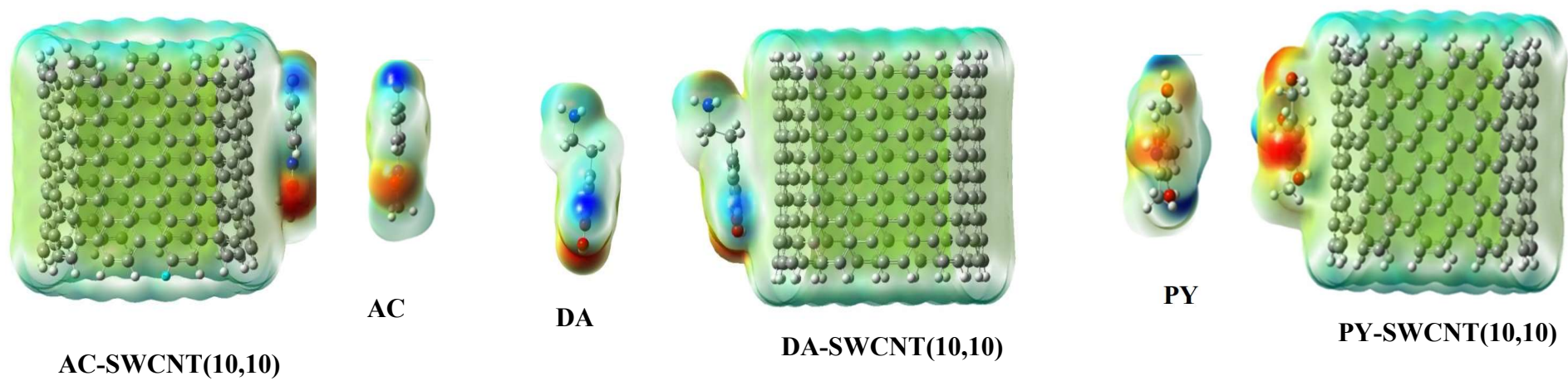


Fig. 2. Isosurfaces for molecular electrostatic potential of individual analytes and their adsorption complexes with SWCNT(10,10). The negative and positive potentials are shown in red and blue colour, respectively.

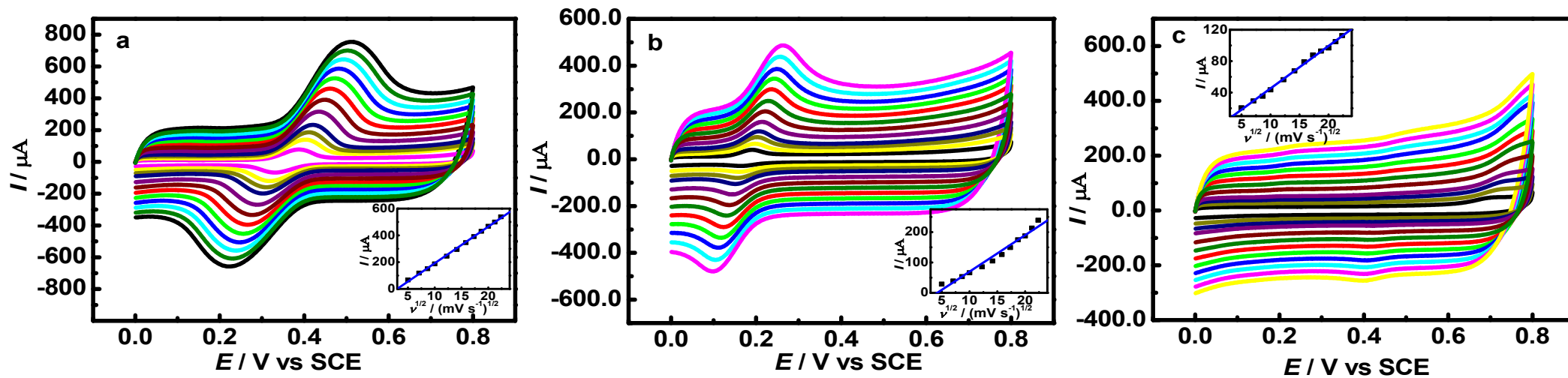


Fig. 3. CV curves of 0.2 mM AC (a), 0.2 mM DA (b) and 0.2 mM PY (c) in 0.1 M pH 7.0 phosphate buffer at GC/SWCNTs electrode with different scan rates. Inset shows the linear relationship between the current and square root of the scan rate.

Fig. 3 shows CV response for the oxidation of AC, DA, and PY at various potential scan rates, as recorded using the GC/SWCNTs electrode. On increasing the scan rate, an increase in the currents is observed (Fig. 3a-3c), with anodic peak currents being directly proportional to the square root of the scan rate (see insets in Fig. 3a-3c), indicating redox processes controlled by diffusion.

Fig. 4 shows the simultaneous oxidation of AC, DA, and PY at bare GC and GC/SWCNTs electrodes. Three distinct peaks for the oxidation of AC, DA, and PY are obtained at the GC/SWCNTs electrode at the oxidation peak potentials 374, 195 and 705 mV, respectively. These oxidation peak potentials are matching well with the oxidation peak potentials of individual oxidation of the respective analytes. These observations specify that the efficiency of individual analyte oxidation process is not affected by the presence of other components in the system. Since the peak potential difference between the individual anodic peaks are distinctly high (c.a., 180 mV between DA and AC and 330 mV between AC and PY), it is expected to carry out the simultaneous determination of these analytes in mixture. At bare GC electrode, for a mixture of AC, DA and PY, only two oxidation peaks are observed with quite low currents and overlapping considerably (see inset on Fig. 4). Thus, bare GC electrode is not appropriate for the quantification of the analytes in presence of each other.

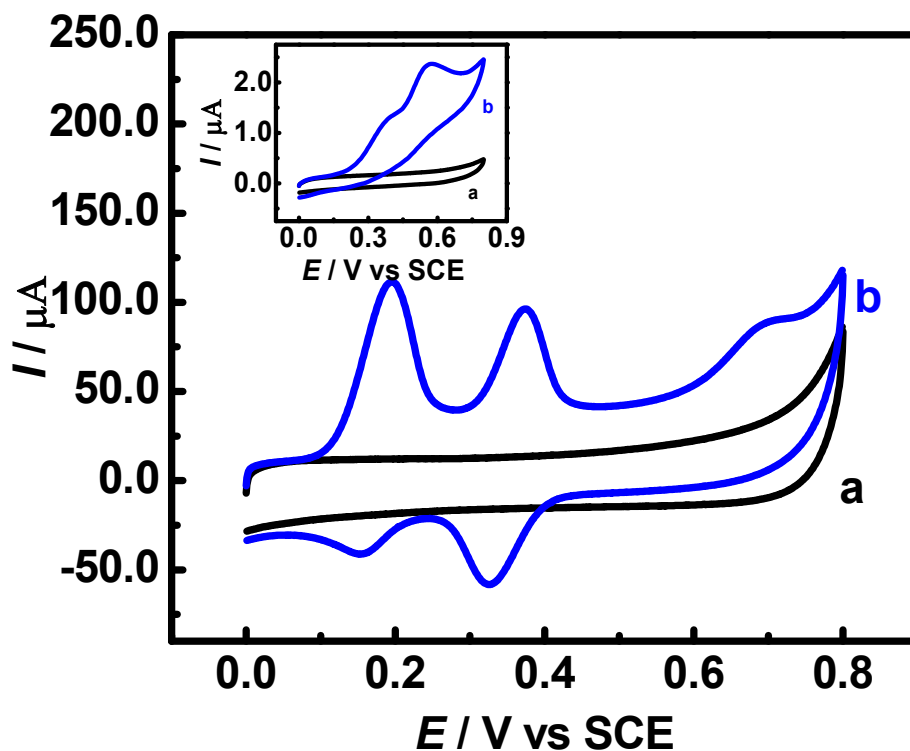


Fig. 4. CV responses recorded at GC/SWCNTs electrode in absence (a) and presence (b) of a mixture of analytes containing AC, DA, and PY (each 0.2 mM) in 0.1 M pH 7.0 phosphate buffer (scan rate: 25mVs^{-1}). Inset shows the same at bare GC electrode.

3.2 Electroanalytical determination of AC, DA and PY

Among the various electrochemical methods, differential pulse voltammetry (DPV) is one of the most sensitive analytical techniques which can be used for the selective electroanalysis of various analytes at trace levels. Typical DPV responses obtained for increasing concentrations of the analytes studied here (AC, DA and PY) at the GC/SWCNTs are shown in Fig. 5. The results are shown respectively for AC (in the 2.0 to 100 μM concentration range, see Fig. 5a), DA (5-750 μM range, see Fig. 5b), and PY (50-1000 μM range, see Fig. 5c). In all cases, when the analyte concentration is incrementally increased there is a regular enhancement in the oxidation peak currents. One can also see from the corresponding calibration plots (insets on Fig. 5) that variations are linear for all the analytes (with an r values of more than 0.99). These plots enable estimating sensitivity values of $7.86 \mu\text{A } \mu\text{M}^{-1} \text{cm}^{-2}$, $3.66 \mu\text{A } \mu\text{M}^{-1} \text{cm}^{-2}$ and $0.31 \mu\text{A } \mu\text{M}^{-1} \text{cm}^{-2}$, respectively for AC, DA and PY.

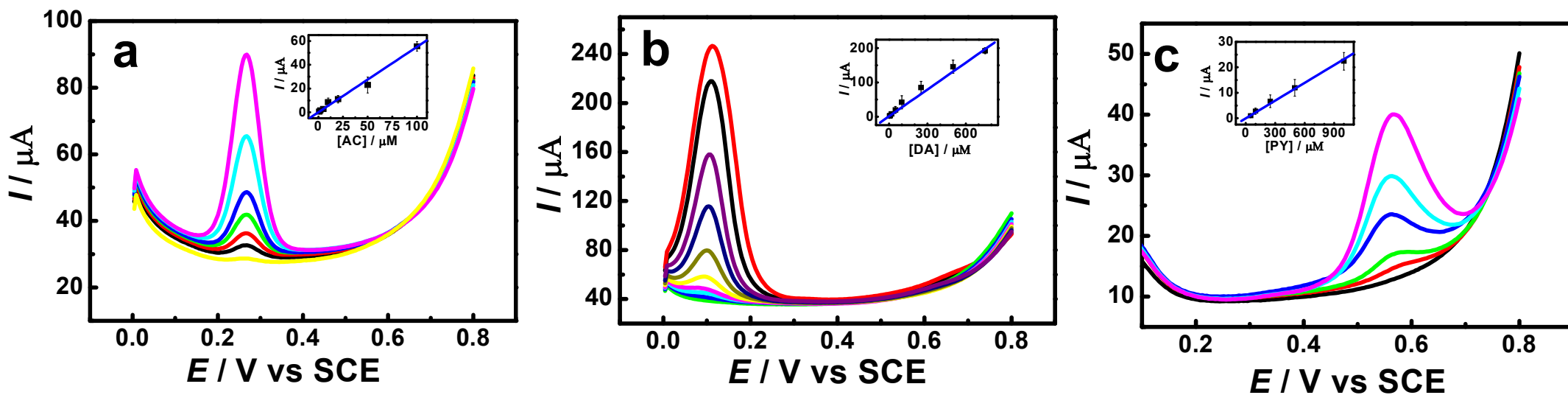


Fig. 5. DPV curves at GC/SWCNTs for various concentrations of AC (a, 2.0-100.0 μM), DA (b, 5.0-750.0 μM) and PY (c, 50.0-1000.0 μM) in 0.1 M phosphate buffer (pH 7.0). Inset shows the respective calibration plot.

Limits of detection (LOD) calculated from $3S/m$ ratios (where S is the standard deviation of the blank and m is the slope of the calibration plot) are respectively $1.1 \mu\text{M}$ for AC, $3.7 \mu\text{M}$ for DA and $7.7 \mu\text{M}$ for PY. This demonstrates the efficiency of SWCNTs in the quantification of all these species taken separately.

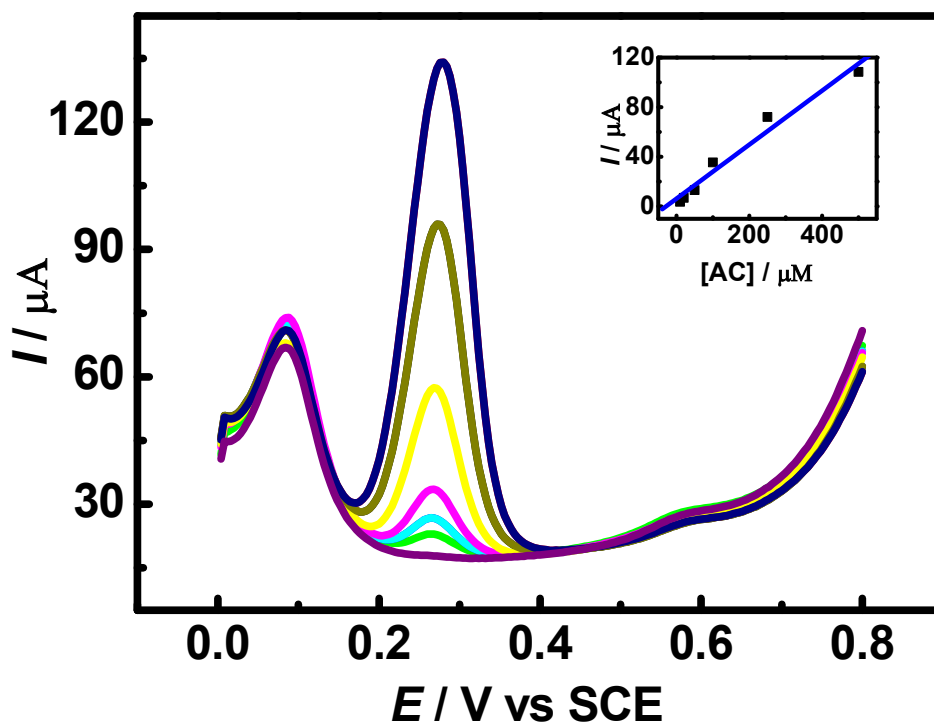


Fig. 6. DPV curves at GC/SWCNTs electrode for the determination different concentrations of AC ($10.0\text{-}500.0 \mu\text{M}$) in presence of DA (0.1 mM) and PY (0.1 mM) in 0.1 M phosphate buffer ($\text{pH } 7.0$).

DPV is also employed for the quantification of AC in the presence of DA and PY (Fig. 6). The concentration of DA and PY is kept constant (0.1 mM each) and the concentration of AC is increased incrementally. As the concentration of AC is increased in the $10\text{-}500 \mu\text{M}$ range, the DPV current response corresponding to its oxidation also increases regularly and no change in the current due to the oxidation of DA and PY is observed (Fig. 6). The inset in the Fig. 6 shows a linear calibration plot with an r value of 0.98 .

Table 1 Comparison of electroanalytical data for the present method along with previously reported methods for the electrochemical oxidation and determination of AC.

Modified electrode ^[c]	Technique used	Medium, pH	Oxidation Potential (V)	Linear range (μM)	Detection limit (μM)	Sensitivity	Reference
Cu-poly-TTCA	CV	Phosphate buffer, pH 7.0	0.48	20 – 5000	5.00	-	[13]
GCE/Nafion/RuO	SW voltammetry	Perchloric acid	0.70	5 – 250	1.20	-	[14]
GCE/C60	DPV	Phosphate buffer, pH 7.2	0.50	50 – 1500	50.00	13.04 $\mu\text{A mM}^{-1}$	[15]
Nano-TiO ₂ /poly(acid yellow 9)	GC	Phosphate buffer, pH 7.0	0.397	12 – 120	2.00	-	[16]
Multi walled carbon nanotube/GCE	DPV	Phosphate buffer, pH 7.38	0.34	5 – 100	2.40	-	[17]
FeTPyPz/GCE	CV	Acetate buffer, pH 3.6.	0.445	4 – 420	1.20	0.046 $\mu\text{A } \mu\text{M}^{-1} \text{ cm}^{-2}$	[18]
GCE/NiHCF-Bt	CV	Phosphate buffer, pH 7.0	0.48	25 – 1000	1.50	0.20 $\mu\text{A } \mu\text{M}^{-1} \text{ cm}^{-2}$	[46]
GC/SWCNTs	DPV	Phosphate buffer, pH 7.0	0.26	2 – 100	1.14	7.86 $\mu\text{A } \mu\text{M}^{-1} \text{ cm}^{-2}$	Present work

^[c]Cu-poly-TTCA = copper terthiophene carboxylic acid polymer; GCE/Nafion/RuO = Nafion@/ruthenium oxide pyrochlore modified glassy carbon electrode; Nano-TiO₂/poly(acid yellow 9) = poly(Acid Yellow 9) coated nano-TiO₂ modified GC electrodes; FeTPyPz/GCE = glassy carbon electrode surface with a Nafion membrane doped with iron tetrapyridinoporphyrazine; GCE/NiHCF-Bt = Nickel hexacyanoferrate incorporated bentonite modified glassy carbon electrode.

3.3 Determination of AC: interference study, stability, reproducibility and real sample analysis

The above data show that the GC/SWCNTs electrode looks promising for the sensitive and selective determination of AC and this is confirmed by Table 1 giving a comparison of the analytical parameters for the determination AC at the GC/SWCNTs together with other reported electrochemical methods [12-17, 46]. As compared to the reported methods [12-17, 46], the present method shows low LOD, high sensitivity and low oxidation potential for the AC determination. Careful comparison of the parameters based on the data in Table 1 infers that the present method is superior over many other methods and therefore this route can be utilized for the selective quantitative recognition of AC even in the presence of DA and PY. The superior performance of the present electrode is mainly due to the different degree of interaction of SWCNTs, with the target analytes. Among the three analytes, AC interacts more with the SWCNTs probably due to the $-\text{NHCOCH}_3$ group of AC [29, 33, 47].

In addition to DPV, the determination of the above analytes can be also performed by amperometry, as exemplified hereafter in the case of AC electroanalysis. Amperometry is an analytical technique in which a constant potential is applied to the working electrode and the resulting current is continuously monitored with addition of target analyte to the stirred supporting electrolyte at certain intervals of time. This approach is well suited to interference studies as it enables the alternative addition of either the analyte or the interference, for instance.

Selectivity of GC/SWCNTs on the determination of AC is evaluated by interference analysis. [Supporting information, Figure S1](#) shows the amperometric determination of AC together with other potential interferent species. Accordingly in the present study, a potential of 0.25

V is applied to the GC/SWCNTs electrode and after 300 s, calculated amount of AC or possible interferences are injected to the supporting electrolyte (0.1 M pH 7.0 phosphate buffer). Whenever AC is injected, an immediate increase in current is observed ([Supporting information, Figure S1](#)) due to the oxidation of AC. Conversely, whenever the possibly interfering species, i.e., alanine, glycine, glucose, uric acid and tyrosine (0.1 mM each) are injected, no change in the amperometric response is observed. Thus, the decreased AC oxidation potential avoids the interference from several oxidizable co-existing molecules, which can be useful in the determination of AC in real samples.

The reproducibility of the AC determination at the GC/SWCNTs electrode is tested by recording the DPV response (ten times at the interval of one minute, see [Supporting information, Figure S2](#)) of the oxidation of 0.1 mM AC. The oxidation peak current for AC shows a relative standard deviation (RSD) of 3.8%, signifying the high reproducibility of the determination. The stability ([Supporting information, Figure S3](#)) of GC/SWCNTs is established by keeping the electrode under room conditions and recording the CV response for 0.1 mM AC determination on the 3rd and 5th days. The CV response retains 96.5% and 87.6% of the current respectively, as that of the initial response observed on the 1st day indicating satisfactory storage stability.

To understand the practicability of the method for real sample analysis the response of GC/SWCNTs electrode towards the determination of AC present in a pharmaceutical tablet, DOLO (a product of Micro Labs Ltd., South Sikkim, India) is estimated. The tablet is carefully crushed into powder and solubilized in a mixture of water and ethanol (70:30). The DPV is recorded and the amount of AC is determined with the previously constructed calibration graph. In addition, the tablet solution is added with known amounts of standard

AC and the recovery percentage is calculated. The results of the recovery analyses are shown in supporting information, Table S1. The average recovery was calculated to be 105.8% which is typical for such analysis. The RSD value for three measurements varies from 2.4 to 8.9% which indicate the acceptable reliability of this method.

4 Conclusions

This work demonstrates the electrochemical quantification of AC, DA and PY using GC/SWCNTs modified electrode. It oxidizes AC, DA and PY at distinctly different potentials with decreased overpotentials due to the different degree of interaction with the SWCNTs. It also shows higher currents for the oxidation which is expected to increase the sensitivity in contrast to bare GC electrode. DFT calculations predict the order of interaction of the target analytes with the SWCNTs as AC > PY > DA which is in accordance with the electrochemical observations. This efficient electrocatalytic oxidation property of SWCNTs leads to the sensitive determination of AC, DA and PY. Interference studies demonstrate that this electrode is appropriate for the analysis of AC in samples of simple matrixes. The sensitivity ($7.9 \mu\text{A } \mu\text{M}^{-1} \text{ cm}^{-2}$), LOD ($1.1 \mu\text{M}$) and linear calibration range ($2.0\text{-}100.0 \mu\text{M}$) obtained in this study are superior to many other methods reported earlier for the determination of AC.

Acknowledgements

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