PANI blended MoS$_2$ decorated GO ternary nanocomposite for efficient electrochemical sensing of crucial components in food and beverages.

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An electrochemical detection dependent on Polyaniline (PANI) blended MoS$_2$ decorated GO (MoS$_2$/PANI@GO) ternary nanocomposite has been developed and used for selective and concomitant determination of Vanillin (VAN), Theophylline (TP) and Caffeine (CAF). The surface morphology and structural properties of the composite are denoted by various scientific methods. The electrochemical behaviour of MoS$_2$/PANI@GO has been investigated by Cyclic Voltammetry (CV) and Differential Pulse Voltammetry (DPV). The electrochemical oxidation (anodic) peaks have been observed at 0.59, 1.1 and 1.36v in phosphate buffer (*p*H 7) for Vanillin, Theophylline and Caffeine, respectively. A good linear current response and limit of detection of 0.043, 0.062 and 0.07 of VAN, TP and CAF, are obtained respectively. The concocted electrode reveals low detection limit, wide linear range, excellent reproducibility, high acuteness and stability. The study is also continued to the analysis of the certain components in the commercial foods and beverage samples.

Keywords: Caffeine, Cyclic Voltammetry, Food Analysis, Theophylline, Vanillin

It is uncompromising to build a sharp, sensible, precise way for detecting active components in food and drinks products to maintain the food safety and quality control. Vanillin (VAN) (4-hydroxy-3-methoxybenzaldehyde) is one class of enchant fragrance compound and it is extensively used as a flavouring and aroma enhancer in food, beverages and drugs[1]. Generally VAN is used in the preparation of food flavours. In every year more than 1.2×10^4 t of VAN is produced, but unfortunately <1% of this is obtained from natural VAN from Vanilla, the remaining is synthesized via industrial process[2]. The most important constituents of VAN (1.6- 2.4% in Vanilla planifoliabeans) are, *p*-Hydroxy benzaldehyde, p-Hydroxy benzoic acid and Vanillic acid[3]. An extreme intake of VAN can incite the capability of damage human liver and kidney[4] and also leading to some other undesired influences such as, headache, sickness, ejection of foods and breathlessness. The maximum usage of VAN is 7mg/100g as per WHO[5]. Theophylline (TP) (1,3-Di-Methyl Xanthine) is one of the utmost broadly used bronchodilators and inhale stimulators for medication of the symptoms of severe and continual asthmatic conditions and it is one of the most often clinical by observe medicine in USA[6]. TP is usually found in some plants and their products. The level of TP in Plasma is below 5 – 20 μg/ml regulate and consider non-therapeutic, during the time above level can cause many undesired side effects and suffer from human health[7]. Caffeine (CAF) (1,3,7-Tri-Methyl Xanthine) is an alkaloid and it naturally occurs. It is an antidepressant to the central nervous process and often used in energy drinks, beverages (Tea, coffee) foods and pharmaceuticals[8]. It is also used in therapeutic treatment of headache, in clubbing with non-steroidal anti-inflammatory drugs and often pain killer pharmaceutical formulation by reason of its diuretic activity[9]. However reports on the study of human and animal revealed that caffeine developed mental and behavioral effects that alike to typical psychomotor stimulant drugs such as amphet amine and cocaine[10]. The suggestion amount of CAF is normally 400mg/day (its equivalent to 4-5 cup of coffee) for healthy adults.

VAN and CAF are two frequent additives and repeatedly co-exist in many refreshment and beverage products which attract large number of customers especially the adults. Similarly TP and CAF both are important alkaloids which are naturally present in black tea, green tea, cocoa[11]. If foods and beverages are consumed together there is a possibility to co-existence of all the three ingredients.

In the current scenario, a various analytical methods have been developed to identify these food

and beverages individually, which includes High Performance Liquid Chromatography (HPLC)[12], gas chromatography[13] and spectroscopic methods[14]. All these modes has some burdens which include endless extraction process before detection, time consuming, expensive and requirement of pretreatment. In comparison, the electrochemical technique[15-17] showed acuteness, high sensitivity, simple instrumentation, low cost, facile mineralization and rapid responses.

Graphene Oxide (GO) with high surface area and high conductivity has established enormous application in variety of areas[18-21]. In addition material preparing, low cost synthesis and capability to form composite materials makes it as an attracting researchers for construct various functional devices such as electrodes[22]. GO is the hydrophilic oxidative derivative of graphene and owing to its oxygen functionalities and uninterrupted electron transfer properties its acts as a sensitive electrode surface[23]. In recent years layered arrangement of transition metal dichalcogenides such as VS$_2$, WS$_2$ and MoS$_2$ has fascinate lots of concerns because of their exclusive chemical and physical properties. Especially the single layer of MoS$_2$ consisting the covalent bonded Mo elements with Sulphur and these layers are sandwiched together weak vander-valls interaction. But the strong covalent bond between the Mo and sulphur atoms contributes to high mechanical strength. So the two dimensional MoS$_2$ has been widely used in a variety of electrochemical applications[24,25]. Conducting polymers such as Poly aniline (PANI) has favor of environmental balance, smooth synthesis and quick doping-redoping. But it exhibits a low stability during charge/discharge mechanism due to volumetric fluctuation which showed the poor rate performance and stability[26,27]. So in this work aimed to incorporate MoS$_2$ and PANI on GO (MoS$_2$/PANI@GO) to design a ternary composite, to promote the electrochemical performance. Already synthesis of rGO-MoS$_2$-PANI ternary composite was reported by Xuani li group for high performance supercapasitors[28]. In continuation of this work we have slightly modified the electrode and fabricated a simple, cheap, reliable and sensitive MoS$_2$/PANI@GO GCE ternary composite for simultaneous electrochemical sensing of VAN, TP and CAF through Different Pulse Voltammetry (DPV). There are very few publications available for the simultaneous determination of VAN and CAF & CAF and TP separately through electrochemical

determination. The best of our knowledge, there are no works on concomitant determination of VAN, TP and CAF. The feasible applicability of the MoS$_2$/PANI@GO electrode was verified through the commercial foods and beverages.

Experimental Section

Powdered graphite, Sodium molybdate, thiourea, aniline, ammonium per sulfate (APS), vanillin, Theophylline, caffeine, were purchased from Sisco Research Laboratory (SRL) Pvt Ltd. Phosphate buffer solution (PBS) was prepared by mixing 0.1 M NaH$_2$PO4 and 0.1 M Na$_2$HPO4.

Synthesis of MoS$_2$ nanoparticle

The hydrothermal synthesis of MoS$_2$ naoparticles was carried out using Na$_2$MoO$_4$.2H$_2$O and thiourea as molybdenum and sulfur precursor, respectively[29]. In a typical synthesis, 0.3 g of Na$_2$MoO$_4$.2H$_2$O were dissolved in 40 mL of deionized water and added continuously thiourea the *p*H adjusted to 6.5 with 80 mL of water. After 1 hr stirring the mixture was transferred to a 100 mL stainless steel Teflon lined autoclave and placed at 180°C for 48 h. The pitch black MoS$_2$ were collected and washed with water and ethanol copious times and dried at 60°C in vacuum oven for 6 h.

Synthesis of poly aniline (PANI)

PANI was synthesized by disperse of aniline (0.9 mL) in 1m HCl (15 mL) and ethanol (10 mL) and deionized water in ice bath under stirring, APS 20 mL was added slowly to it. After 12 h polymerization in ice bath under magnetic stirring, the suspension of PANI was filtered and washed with water and ethanol. Finally PANI was filtered under vacuum and dried at 60°C for 24 h.

Synthesis of MoS$_2$/PANI@GO ternary composite
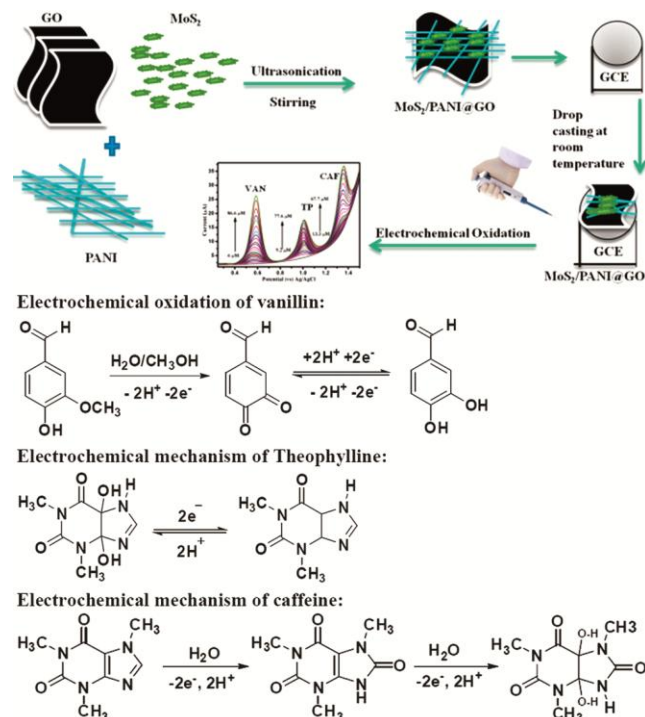
The MoS$_2$/PANI@GO ternary composite was prepared by simple ultrasonication mode. First the Graphene Oxide (GO) was prepared by oxidation of Graphite powder by a modified Hummers method[30]. GO (0.05g) was taken and dispersed in 20 mL deionized water by ultrasonication for 45min. Then 0.04g of MoS$_2$ and PANI were added to the above solution and then ultrasonicated for 1 h. Subsequently the composite were transferred a Teflon lined stainless steel auto clave for 12 h hydrothermal treatment at 180°C to obtain the black colour composite was filtered and washed with water and ethanol and then dried at 80°C in a vacuum oven.

Fabrication of MoS₂/PANI@GO ternary composite modified GC Electrode (GCE)

GCE was polished to get glass-like surface on a micro cloth pad with various grades of alumina powder (1.0, 0.5 and 0.05 μm). After polished, the GCE was ultrasonically cleaned in water and ethanol in order to remove a surface residue. Finally, the GCE was rinsed in deionized water and dried at room temperature. After that 10μL of composite solution (MoS₂/PANI@GO) was placed on the electrode surface and dried at room temperature (26-28°C) (Scheme 1). For comparison, MoS₂/GCE, GO/GCE and PANI/GCE, were also prepared under the same condition and evaluated.

Analytical procedure

Phosphate buffer solution (PBS) pH 7 used as a non reactive supporting electrolyte for electrochemical measurements. After being 10 mL of pH 7 PBS in the electrochemical cell, the required volume of VAN, TP and CAF was added by a micropipette. Finally, the results of Cyclic Voltammetry (CV) and Differential Pulse Voltammetry (DPV) were obtained using HCH instrument electrochemical work station with a three electrode system. Glassy Carbon Electrode (GCE) has working electrode (0.03 cm^2), and Reference electrode (Silver Silver Chloride Electrode (Ag/AgCl). The counter Electrode was platinum wire.

Scheme 1 — Schematic Illustration of the fabrication and sensing process of MoS₂/PANI@GO nanocomposite modified GCE.

Results and Discussion

Morphological analysis of MoS₂/PANI@GO ternary composite

The morphology of the materials was examined by FE-SEM. The FESEM image of GO, shown in Fig. 1 (a) showed a layer structure with cloth like morphology for the free one. Formation of layers its due to π−electronic clouds and the oxygen containing functional groups like –OH, -COOH and epoxides. Similar morphology for GO was reported in the literature[31]. The FESEM image of MoS₂ shown in Fig. 1(b) showed a spherical porous sphere built with tiny petals of MoS₂. The petals were randomly organized, in the formation of spheres, the porous structure advantages as it would enable diffusion of electrolytes through the matrix during the study of cyclic Voltammetry (CV). The FESEM image of Polyaniline (PANI) Fig. 1(c).showed tiny rods associated with porous. Both MoS₂ and PANI have inter connected with porous. The FESEM image of MoS₂/PANI@GO composite is shown in Fig. 1 (d). Its showed thick layer morphology and individual morphology of GO, MoS₂ and PANI were not separately retained. So, they must be thoroughly mixed the formation of thick layers. The surface was not smooth and there might be tiny porous in each layers.

XRD, Raman and FT-IR analysis of MoS₂/PANI@GO ternary composite

The XRD patterns of GO, MoS₂, PANI and MoS₂/PANI@GO ternary composite are shown in Fig. 2A. The diffraction peaks recorded at 2θ value of 14.1^0, 33.1^0, 53.1^0 and 58.9^0 can be assigned to (002), (100), (106) and (110) crystals faces of MoS₂[32,33]. Similarly the diffraction peaks at 2θ = 11.13^0 is due to (002) of GO[34]. The diffraction peaks of PANI located at 2θ value of 14.8^0, 20.3^0, and 25.3^0 are

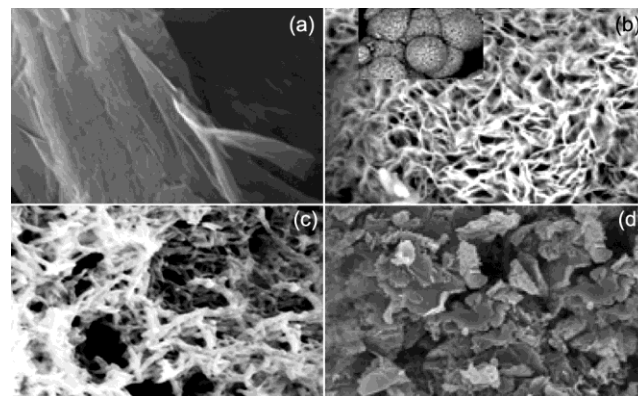

Fig. 1 — FE-SEM images of (a) GO, (b) MoS₂ (c) PolyAniline (d) MoS₂/PANI@GO ternary composite.

corresponding to (011), (020), and (200) of PANI[35]. The peaks of MoS$_2$, PANI, and MoS$_2$/PANI@GO the reflections of the individual components. The reflection due to PANI was dominating over the others. So, it could be inferred, that the rods of MoS$_2$ must form, the upper most PANI of the composite. The peak position of GO is shifted towards lower angle of reflection, hence the layers of GO might be little separated due to interaction with an others components. In the case of PANI the reflection was shifted towards higher angle in the composite, hence PANI crystals must be little compressed by the overlaying ingredients. Shift in the peak position of MoS$_2$ was also evidenced in the XRD patterns.

Figure 2B shows the characteristic Raman peak of MoS$_2$ detected at 358 and 425 cm^{-1} due to E$_{2g}$ and A$_{1g}$ modes of MoS$_2$[36,37]. The Raman spectra of GO showed two predominant peaks at 1323 and 1590 cm^{-1} which are corresponding to D (disorderly defect structure) and G (sp^2-bonded carbon atoms) bands respectively. The peak at 535 cm^{-1} is assigned to out of plane PANI ring bend[38]. The peaks at 596 and 813 cm^{-1} are characteristic of the benzenoid ring deformation, and out of plane vibration of aromatic rings[39]. Other peaks at 1138, 1119, 1454 and 1685 cm^{-1} are related to C-H vibration, C-N vibration, C=N of the di-imine units, C=C band C-C band respectively[36-39].

Figure 2C shows the FT-IR spectra of GO, MoS$_2$, PANI and MoS$_2$/PANI@GO ternary composite. PANI showed intense peaks at 1189, 1286, 1397, 1532 cm^{-1} due to C=N stretching, C-N stretching of the secondary amine, and the aromatic C=C stretching vibrations of the benzenoid and quinonid rings, respectively[40]. The broad band at observed at 3402 cm^{-1} is due to the stretching vibration of the O-H group present in the GO, similarly the peaks corresponding to C-O and C=C groups were observed at 1033 and 1669 cm^{-1} respectively. There are peaks at 632, 835, 969, 1397, 1629 cm^{-1} attributed to MoS$_2$[41]. The band at 528 cm^{-1} is due to the S-S bond[42]. And that peak at 3399 cm^{-1} belongs to the O-H stretching vibration of water. The MoS$_2$/PANI@GO ternary composite was complete by free of water there were no peaks below 2000 cm^{-1}.

Electrochemical Characterization of MoS$_2$/PANI@GO ternary composite

Cyclic Voltammogram (CV) is the most widely used analytical technique for the study of electrochemical reactions. In general, CV method has been applied to investigate the electrochemical
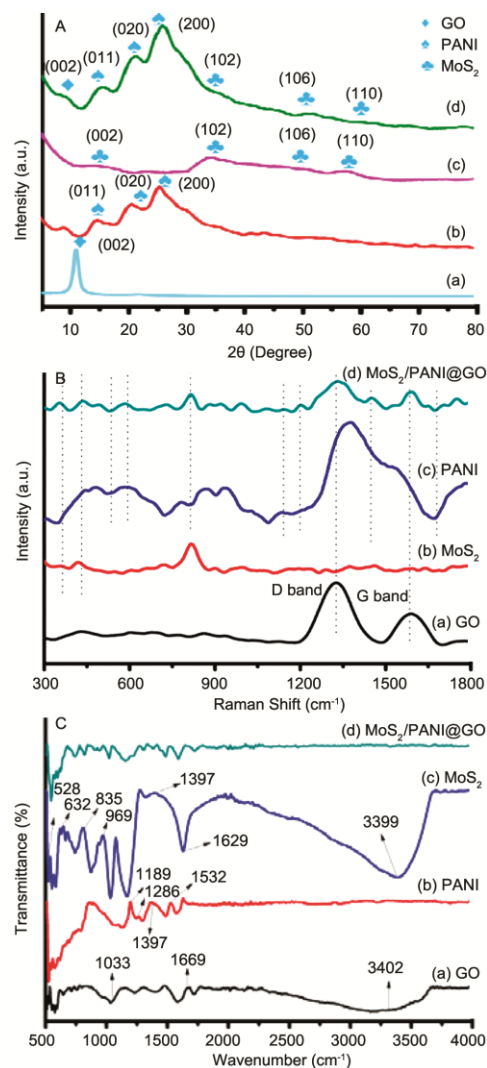

Fig. 2 (A–C) — (A) XRD patterns of (a) GO, (b) PANI, (c) MoS$_2$ and (d) MoS$_2$/PANI@GO ternary composite; (B) Raman spectra of (a) GO, (b) MoS$_2$, (c) PANI and (d) MoS$_2$/PANI@GO ternary composite; (C) shows the FT-IR spectra of GO, MoS$_2$, PANI and MoS$_2$/PANI@GO ternary composite; FT-IR spectra of (a) GO, (b) PANI, (c) MoS$_2$ and (c) MoS$_2$/PANI@GO ternary composite.

behavior of modified electrodes in the presence of different analytes. Fig. (3). show the CV response of (a) bare GCE, (b) GO-GCE, (c) MoS$_2$-GCE, (d) PANI-GCE and (e) MoS$_2$/PANI@GO GCE electrodes VAN containing 0.1M of PBS at a scan rate 50mV/s. For the bare GCE the oxidation peak of VAN was unnoticeable. In all the voltammograms, a single oxidation peak was reveal for VAN, with no corresponding reduction (cathodic) peak in the reverse potential scan suggesting the irreversibility of the electrode reaction. In comparison to bare GCE, the peak current response of VAN increased at the
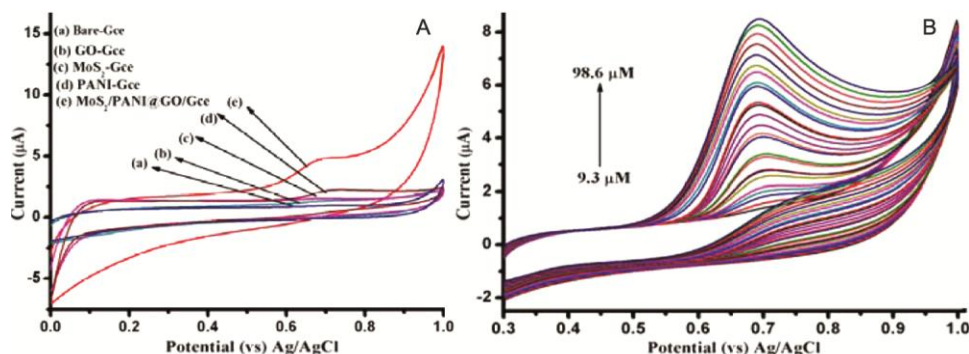
Fig. 3(a) — Cyclic voltammogram of (a) bare GCE, (b) GO-GCE, (c) MoS₂-GCE, (d) PANI-GCE and (e) MoS₂/PANI@GO GCE electrodes in the presence of 9.6μM VAN containing 0.1m of PBS at scan rate 50mV/s. Fig5(b) MoS₂/PANI@GO electrode at different concentrations of VAN.

modified electrodes with the maximum response for the ternary composite modified electrode (curve e). VAN oxidation potentials observed at different electrodes are shown in Table 1

The oxidation of VAN on MoS₂/PANI@GO electrode occurred at a lower potential, and higher electrical conductivity is due to the MoS₂ which has tiny petals structure decorated on graphene sheet[43]. MoS₂/PANI nanocomposite absorbs the analytes and exhibit excellent electrocatalytic performance[44]. The results demonstrate that MoS₂/PANI@GO possesses the electrocatalytic activity towards the oxidation of VAN. More over the detailed electrocatalytic activity of MoS₂/PANI@GO electrode was studied through CVs with different VAN concentration Fig. (4A) b. shows the linear range from 9.3 to 98.6μM.

Effect of *p*H and Scan rate

A redox reaction mainly depends on the *p*H of the buffer solution. The *p*H can impact the peak outline, peak potential and peak current of the modified electrode and also it is useful to estimate the proton to electron ratio involved in the electrode reaction. From the result, it is evidently proven that the peak current decreased with the increase in *p*H from 3 and 5 due to the involvement of protons. More precisely, the peak potential also shifted towards higher potential value. Similarly, the peak current decreased at pH 9.while, the higher oxidation current with lower potential was obtained at *p*H 7. Thus the *p*H 7 was chosen for subsequent analytical experiments. In addition, the peak potential (Ip) shifted negatively with the increase in the *p*H[45]. Fig. (4A) shows the linear relationship between the anodic peak potential and pH with linear regression equation of EP(V) = 0.0313pH + 0.895 (R² = 0.9595). According to the following the formula of Nernst equation[46].
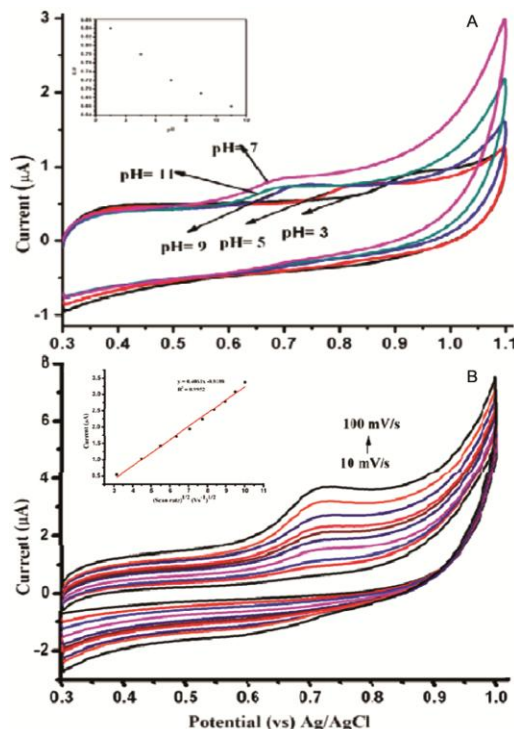

Fig. 4. (a) — Cyclic voltammograms of the effect of scan rates in 0.1M PBS at (a) MoS₂/PANI@GO GC electrode and (b) plot of square root of the scan rate vs Anodic Current.

Table 1 — VAN oxidation potentials observed in different electrodes

Modified Electrode	Epa (V)	Ipa (A)
Bare GCE	0.780	0.99
GO-GCE	0.70	1.34
MoS₂-GCE	0.71	1.62
PANI-GCE	0.716	2.27
MoS₂/PANI@GO	0.68	4.67

$$dEp/dpH = 2.303 \, mRT/nF$$

where F is the Faraday constant (96485 C/Mol), R the universal gas constant (8.314 JK⁻¹Mol⁻¹),

T temperature (298K), m the number of protons and n the number of electron involved for VAN oxidation. The value of m/n was equal to 1.96 which approximately equal to 2[47]. It showed that the number of electrons and protons in the oxidation of VAN is equal.

In order to study the kinetics of the VAN oxidation at MoS$_2$/PANI@GO GCE the electrochemical response was measured from 10 to 100mV/s scan rate. The CV technique was employed to probe the effect of scan rate potential and the oxidation of VAN. In Fig. 4B(I) reveals for the relationship between the scan rate ($v^{1/2}$) and current response (I) as well as the oxidation potential (Ep) 9.2μM of VAN at the MoS$_2$/PANI@GO in 0.1m of PBS at *p*H7). The oxidation peak current increased with the increases in the scan rate. The reduction peak of VAN was not observed in the reverse scan, and the oxidation peak potential shifted to more positive value. Therefore, it is suggested that the electro chemical reaction of VAN on the MoS$_2$/PANI@GO GCE an irreversible process. Plot of anodic peak current (vs) square root of scan rate ($v^{1/2}$) is shown fig 4B(II). Linear regression equation Ipa (μA) = 0.4061($v^{1/2}$/mV$^{1/2}$/s$^{1/2}$ - 0.818 (R^2 = 0.9952) suggest that the oxidation of VAN is diffusion controlled[48].

Voltammetric determination of Vanillin

The relationship among the oxidation peak current and the concentration of VAN was investigated by DPV. The DPV has leads to increase the sensitivity

and high resolution in quantitative analysis compared to the conventional CV. Fig. (5) shows that under the optimized experimental condition, the oxidation peak current linearly increased with the VAN concentration in the range from 6.2 to 129μM. The linear regression equation Ip(μA) = 0.1817x -0.328 with correlation coefficient R^2 = (0.9978) is obtained. The detection limit was equal to 0.043μM at the signal to noise ratio (S/n) of 3. The analytical performance was study with previously reported sensors in Table 2

The main feature of the present investigation is the designed sensor is able to oxidize VAN, TP and CAF simultaneously with large peak-to-peak potential separation. It was difficult to resolve the potentials of these three analytes through CV because overlapping of oxidation peak currents. The DPV method was employed to resolve peak potential of VAN, TP and CAF in where charging current and background current were completely eliminated by this method. In the first the concentration of VAN was increased from 6.9 to 114μM while the [TP] (9.2μm) and CAF (13.3μM) were kept constant. The DPV results are illustrated Fig 5B and the observed peak revealed no change in peak current for TP and CAF while increasing the concentration of VAN. Confirms that there is no molecular inter effect in the analytes. The oxidation peak current of VAN increased linearly with the increase in the concentration (Fig 5B inset) showed a linear relationship Ip(μA) = 0.194 (VAN
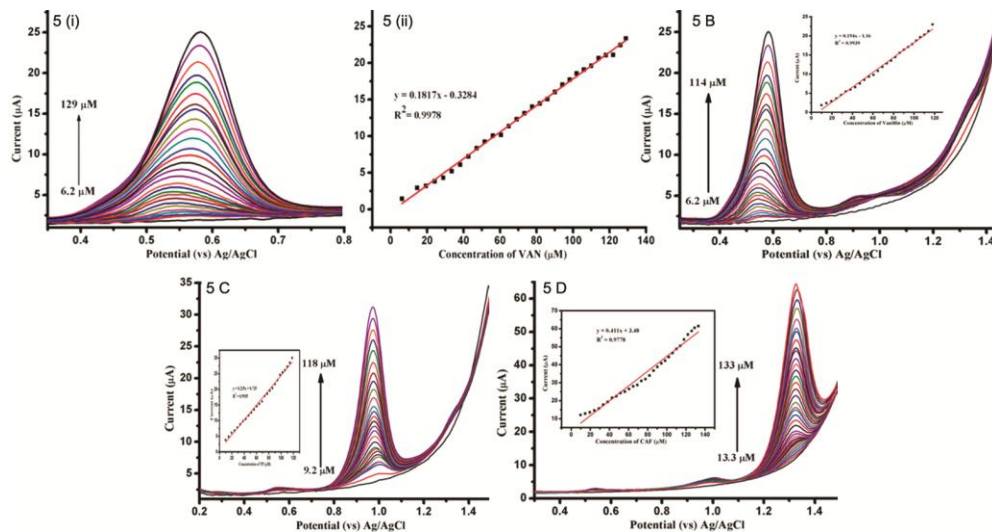

Fig. 5A (a) DPVs of the effect of [VAN] in 0.1 M PBS at MoS$_2$/PANI @GO GC electrode (b) linear relationship between the concentrations of VAN vs anodic peak current; (b) DPVs of the effect of [VAN] at MoS$_2$/PANI @GO GC electrode with a fixed concentration of TP and CAF, and their plot of concentration vs peak current (inset); (c) DPVs of the effect of [TP] at MoS$_2$/PANI@GO GC electrode with a fixed concentration of VAN and CAF, and their plot of concentration vs peak current (inset); (d) DPVs of the effect of [CAF] at MoS$_2$/PANI@GO GC electrode with a fixed concentration of VAN and TP, and their plot of concentration vs peak current (inset).

Table 2 — Comparison of different analytical performance of MoS_2/PANI@GO GC Electrode with other reported electrode

Electrode	Analyte	LOD (μM)	Sample	Ref
Graphene/GCE	VAN	0.056	Food sample	50
Poly(Acid Chrome Blue K) GCE	VAN	0.032	Food Sample	51
GNP/GCE	VAN	0.012	Food Sample	52
AuPd-GR GCE	VAN	0.02	Food Sample	53
LMC/Nafion flim modified electrode	CAF + TP	0.37 + 0.47	Biological/Tea sample	54
Poly(Alizerin Red) GCE	CAF + VAN	0.06 + 0.8	Beverage and Sugar	55
MnO_2 nanosheets/ionic liquid functionalized graphene	TP	0.1	Drug	56
Poly(CTAB)/GCE	TP	0.44	Urine Samples	57
boron-doped diamond electrode	CAF	0.15	Beverage	58
	VAN	0.043	Food and Beverage Samples	This Work
MoS_2/PANI@GO GC Electrode	TP	0.062		
	CAF	0.07		

Compound: VAN, vanillin; TP, Theophylline; CAF, caffeine.
Electrode: Au, gold; GCE, glassy carbon; CPE, carbon paste.
Modifier: GNP, Graphene nanoflake; MWCNT, Multi wall carbon nanotube; LMC, Large Mesoporous Carbon; MoS2, Molybdenum-disulfide; PANI, Polyaniline; GO, Graphene Oxide, CTAB, Cetyl Trimethyl Ammonium Bromide
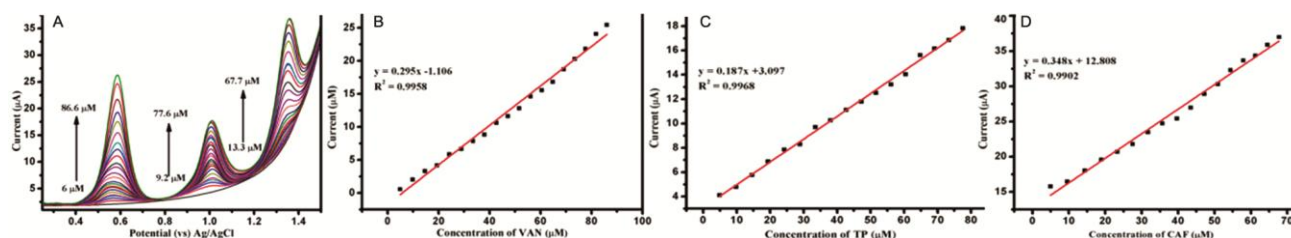

Fig. 6 — DPVs for simultaneous determination of vanillin, theophylline and caffeine at MoS_2/PANI@GO electrode and their plot of concentration vs current.

μM) -1.16 with corresponding correlation coefficient R^2= 0.9939. The limit of detection was equal to 0.043μM. In the second experiment, the concentration of TP was varied while the concentration of VAN and CAF kept Constant. Fig. 5C inset shows the increase the concentration of TP linear relationship 9.2 to 118μM as Ip(μA) =0.235(TP μM) + 0.735 with R^2 = 0.9939 and the limit of detection was equal to 0.065μM. It is important to mention that the oxidation of TP occurred at 0.98V at pH =7 through lose of a proton and electron as shown in the following reaction, and a similar observation was also reported in the literature[49]. Similarly, in the third case the concentration of CAF was varied and VAN and TP keep the constant. Fig. 5D. Inset shows linear relationship in the range of 13.3 to 133μM with corresponding the linear regression equation Ip (μA) = 0.411(CAFμM) + 3.48 R^2 = 0.9778. The limit of detection was equal to 0.07μM. in CAF the initial step of the reaction is a two electrons and two proton oxidation of the C-8 and N-9 bond giving substituted uric acid. Two electron and two proton oxidation of 4,5 diol analogs uric acid occurs, which is in agreement with previous reported[57,58].

Simultaneous determination of VAN, TP and CAF was carried out and the observed DPV electrocatalytic oxidation of VAN, TP and CAF in different concentrations at MoS_2/PANI@GO GC Electrode is shown in Fig. (6). The oxidation peak current VAN increased linearly 6 to 86.8μM with the linear regression equation Ip (10^{-6}) = 0.296x -1.106 (R^2 =0.9958). Similarly the TP peak current increased linearly in the range from 9.2 to 77.68μM with the linear regression equation Ip(μA) = 0.187x +3.07 R^2=0.9968 and for CAF has 13.3 to 67.7μM with linear regression equation was Ip(μA) = 0.348+12.808 R^2=0.9902. These results showed well defined oxidation peak potentials 0.6V, 0.9V and 1.35v for VAN, TP and CAF, respectively. Hence, the concomitant determination of these analytes is feasible without any interference using this ternary composite electrode.

Interference study

The effect of selected intrusive compounds which may unite VAN, TP and CAF was also inspected under the same experimental condition. The tolerance limit was taken as the high concentration of foreign

substance, which caused roughly $\pm$ 5 % relative error in the determination of these compounds. It was found that 10 fold surplus of the common ions such as $Ca^{2+,}$ $Mg^{2+,}$ Zn^{2+}, K^+, Na^+, Cl^-, Ca^{2+}, Fe^{3+}, SO_4^{2-} and NO^{3-} did not significantly interfere with the DPVs. The result is illustrated in Fig. 7 and very little change in the oxidation potential was observed. Hence, the oxidation potentials of the analytes proved very negligible interference due to such added components. Hence, the electrode is verified as much selective towards oxidation of VAN, TP and CAF.

Stability, reproducibility and repeatability

The stability of the MoS$_2$/PANI@GO GC electrode was evaluated through CV. For evaluating stability, the electrode was examined for the determination of VAN, TP and CAF in the same concentration under the same condition. The electrode was started in 0.1 m of PB solution containing 100 µL 0.01 mM of VAN at room temperature. Even after one week no oblivious decrease in current was obtained thus illustrating the electrodes stability. The repeatability was studied for five continuous experiments. It showed RSD 3.6%, thus confirming the reproducibility. Fig. (8). All these results proved that the electrode can be employed for practical application.

Practical Application

The MoS$_2$/PANI@GO modified GCE was tested for food and beverage samples like biscuit, black tea and cola to evaluate practical applicability. The samples were purchased from Chennai local market. The cola sample was used directly without any *p*H adjustments. For vanilla biscuit sample 6g was ground in an agate mortar. with 10 mL of the PB solution *p*H7 and 1% ethanol. For the tea sample 2g was dispersed in hot water and cooled at room temperature. It was shaken vigorously for 10min. The vacuum filtrated and diluted 50 ml with water. 10µL of sample solution and 10 ml of *p*H 7 PB solution, the DPV curve was recorded from 0.2 - 1.5V. Cola beverage sample one oxidation peak appeared at

1.31V. However for Vanillin contain biscuit also evaluated in DPV technique for 10µL of biscuit sample we obtained only one oxidation peak potential 0.6. These results are nearly matched with previous simultaneous results. For the black Tea sample two oxidation potentials 1.15V and 1.31V were noticed. Each sample was determined three times. The Relative Standard Deviation (RSD) revealed good precision, and the results are reported in Table 3. in addition the recovery of VAN, TP and CAF standard was performed to testify the accuracy of the method.
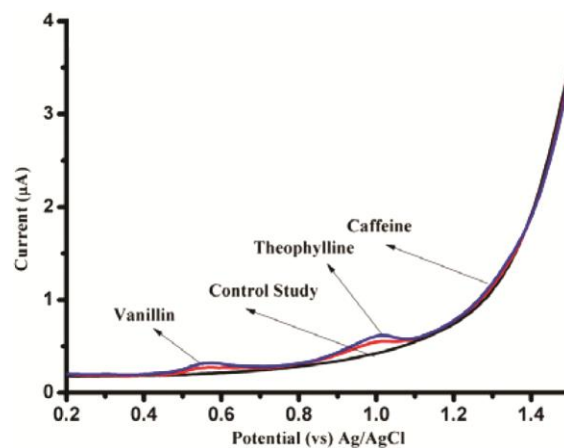

Fig. 7 — DPVs of MoS$_2$/PANI@GO electrode (black curve), MoS$_2$/PANI@GO with 6.2µM VAN, 9.2 µM TP, 13.3µM CAF (red curve) in absence and presence (blue curve) of K+, Na+, Cl$^-$, Ca^{2+}, Mg^{2+} ,Zn^{2+}, Fe^{3+}, NO^{3-} and SO$_4^{2-}$.
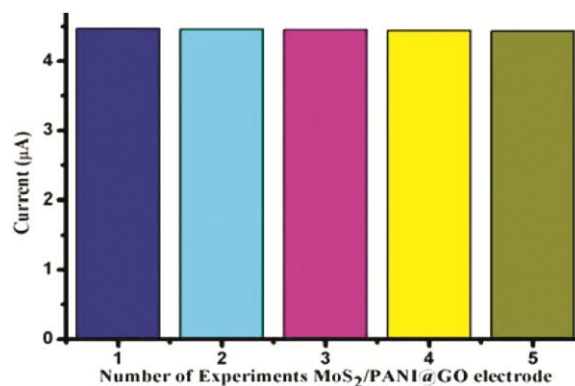

Fig. 8 — Repeatability of MoS$_2$/PANI@GO electrode for 5 consecutive experiments

Table 3 — Analysis of Vanillin, Theophylline and caffeine in real samples with MoS$_2$/PANI@GO GC Electrode

Samples	Original(µM)			Added (µM)			Found (µM)			Recovery (%)		
	VAN	TP	CAF	VAN	TP	CAF	VAN	TP	CAF	VAN	TP	CAF
S1	---	---	9.2	10	5	10	9.3	4.3	19.1	93	86	101.2
S2	9.6	--	--	5	10	15	14.2	11.1	16.3	101.2	99.59	99.56
S3	--	1.92	9.5	5	6	20	4.33	8.11	29.3	93.5	99.55	101.66

S1, Cola-sample; S2, Vanillin biscuit; S3, Black Tea-sample

-- Not detected

The recovery varied as 99.52, 99.66 and 101.59% suggesting that this method is effective and reliable.

Conclusion

We have fabricated MoS$_2$/PANI@GO for the electrochemical sensing of VAN, TP and CAF. A high increase in the oxidation currents of VAN, TP and CAF with their distinct peak potentials was observed. Compared to the previous reports high sensitivity selectivity and lower limit of detection 0.043, 0.064 and 0.07 VAN, TP and CAF respectively. The fabricated electrode was also used to examine practical samples cola, vanillin containing biscuit and tea for quantification of VAN, TP and CAF, and results confirm the applicability of the present modified electrodes as sensor for practical applications.

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