Indian Journal of Chemistry
Vol. 59A, September 2020, pp. 1285-1291

Modification of glassy carbon electrode with trigona carbon nanopetals/ferrocene/gold nanoparticles nanocomposite for electrochemical detection of dopamine

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Received 14 April 2020; *accepted 30 July 2020*

In this study, we have synthesized a composite using carbon material derived from bio-inspired onion peel morphology like 2D trigona carbon nano petals (TCP) incorporated with ferrocene (FC). The FC is added with the purpose of improving the electrochemical behaviour of TCP. Further, to increase the number of electrochemically active sites in the composite, gold nanoparticles (AuNPs) were again decorated on TCP/FC, and thus derived electrochemically active TCP/FC/AuNPs nanocomposite. We have characterized the properties and surface morphology of this nanocomposite through spectroscopic and microscopic techniques. Further, using this nanocomposite for surface modification of glassy carbon electrode, we have developed an efficient GCE-TCP/FC/AuNPs electrode. The electrochemical efficiency of this electrode has been inspected through sensing and quantification of pharmaceutically valuable biomolecule dopamine through CV, DPV and square wave voltammetry techniques. The observed CV results reveals that the newly designed GCE-TCP/FC/AuNPs electrode has an ability to detect the dopamine with wide linear range of concentration from 5.96×10^{-6} to 0.1×10^{-4} M and its limit of detection was 2.9×10^{-6} M under 0.1 M phosphate buffer medium (pH 7.0). Therefore, it is important to mention here that this newly fabricated electrode can very well be used for real time sample analysis for sensing and detection of dopamine as it plays a key role in the neurotransmission and causes several diseases.

Keywords: Dopamine hydrochloride, Electrochemical detection, Ferrocene, Trigona carbon nano petals (TCPs)

Carbon materials, graphene, graphene oxide, carbon nanotubes, etc., have engrossed researchers in the field of nanotechnology[1-5]. The good electrical conductivity, huge surface area, and chemical stability of these materials find several applications in catalysis, energy storage, fuel cells, water purification and biomedicine[6-8]. Among the various carbon materials, 2D carbon nano petals have more advantages because of the arrangement of carbon atoms in a conjugated hexagonal network as that of graphene oxide[9-11]. Although, covalent or non-covalent functionalization of the surface of 2D carbon nano petals can enhance the physicochemical features of 2D carbon materials, owing to synergetic effects and generation of new characteristics, which cannot be exhibited by 2D carbon nano petal structures alone, it could be either functionalized or covalently bonded with some other materials with high molecular receptors or sensing ability. However, the difficulties in synthesis and cost-effective functionalization of 2D carbon are limited to their wide range of applications.

In the present study, in order to make it affordable we made an attempt on low-cost synthesis of 2D carbon materials derived from bio-resources[12-16]. Though, 2D carbon materials are derived from various bio-resources, onion peel[17] is a significant source of carbon which has complex biochemical composition (flavonoids, quercetin and anthocyanin) exhibiting huge benefits. Considering the electrical and piezoelectric properties[18-22], we planned to examine the sensitivity and detection ability of onion peel (OP).

Ferrocene is one of the most stable organometallic compounds with a sandwich-structure and the most useful one among metallocenes[23-25] due to its reversible redox properties. In the field of electrochemical detection, ferrocene has a promising application prospect in view of its impact as a component of molecular receptors and sensing materials. Ferrocene has good thermal stability and tolerance toward oxygen due to the interaction between the iron atom and the cyclopentadienyl ring. This interaction also facilitates the synthesis of various ferrocene derivatives. Additionally, ferrocene has a lower oxidation potential to lose an electron (0.40 V) on account of the oxidizability of its iron atom

and two stable redox states (ferrocene and ferrocenium). Hence, considering these unique properties of ferrocene, it is decorated on reduced trigona carbon nano petals (rTCP) to enhance the electrochemical behaviour and further stabilized with AuNPs[26-28] to increase the active sites on the carbon surface. If they are properly designed, ferrocene derivatives and ferrocene based polymers and dendrimers which have a fast electron-transfer rate[29-31] and exhibit excellent charge/discharge properties, can be applied in molecular recognition and as electrochemical sensors.

Quantitative determination of dopamine in physiological fluids is of great interest. This molecule plays an important role in neurotransmission and other physiological processes[32]. Lower levels in dopamine causes diseases, such as Parkinson's disease, schizophrenia, etc., Different analytical techniques have been used to detect dopamine in biological samples, such as high-performance liquid chromatography (HPLC)[33], capillary electrophoresis[34], HPLC coupled mass spectroscopy[35], electrochemistry[36] and field-effect transistors[37]. The electrochemical approach is attractive as it is easily scalable, cost effective method and allows dopamine determination with fast response time using differential pulse voltammetry. Recently, metal nanoparticle stabilized CNTs or graphene-modified electrodes have been reported to exhibit fast electron transfer rate, low background current, low ohmic resistance, low over-potential and negligible surface fouling. To overcome these properties, ferrocene decorated carbon nano petals which show enhanced metallic behaviour and exhibit excellent biocompatibility.

In this study, we have aimed to stabilize AuNPs on ferrocene decorated carbon nano petals which have more active surface area, and thus should result in enhanced electrocatalytic properties. This nanocomposite material can be used as a modified electrode for effective detection of dopamine hydrochloride.

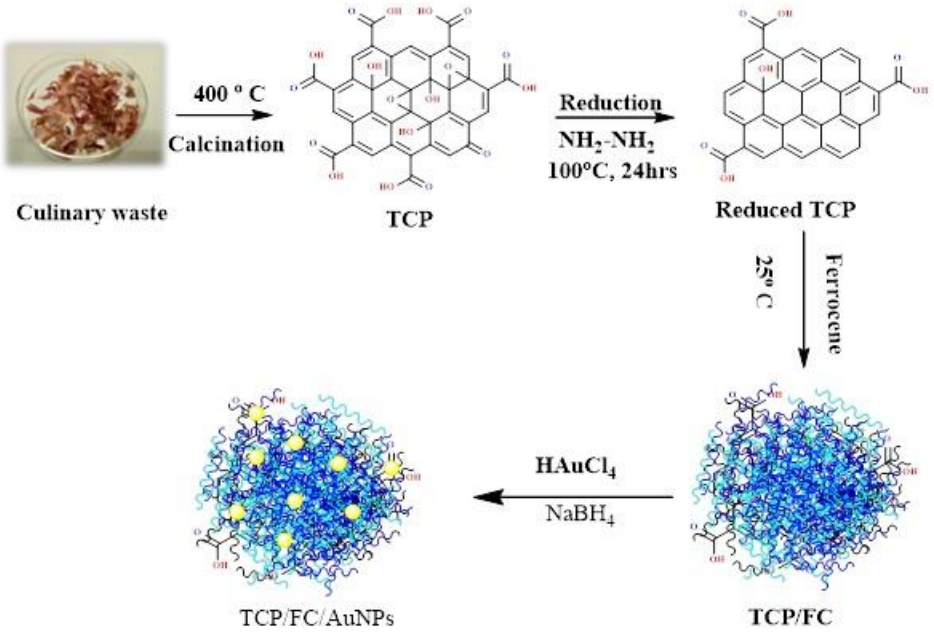
Materials and Methods

Materials

Ferrocene (Sigma-Aldrich), dopamine hydrochloride (Sigma-Aldrich), disodium hydrogen phosphate (Sigma-Aldrich), sodium dihydrogen phosphate (Sigma-Aldrich), hydrazine hydrate (SRL), ethanol (SRL) were used without further purification. De-ionized water obtained by double distillation was used for preparation of various solutions.

Synthesis of TCP/FC

Trigona carbon nano petals (TCP) were synthesized from onion peel (OP), which was initially washed with de-ionised water, ethanol (4-5 times) and finally calcined at 400°C in inert atmosphere. They were reduced with hydrazine hydrate, and thus produced reduced Trigona carbon nano petals (rTCP). rTCP (1.0 mg) and ferrocene (1.0 mg) in ethanol were added to a mortar and ground well for about 1h. then the mixture was dried at 60ºC under vacuum to obtain a solid. (Scheme 1).



Scheme 1— Schematic illustration for the synthesis of TCP/FC/AuNPs Nanocomposite

Synthesis of TCP/FC/AuNPs nanocomposite

TCP/FC (25 mg) was dispersed in a sonicator with 20 mL ethanol in a 50 mL round bottomed flask. $HAuCl_4$ (0.25 mg) was added to it and sonicated for 10-15 min. It was stirred with a magnetic stirrer for about 3 h, and then added 2 mg of $NaBH_4$ and stirred again for 1 h. Finally, the obtained solid was washed with ethanol and acetone. The obtained solid was dried at room temperature.

Stock solution of dopamine hydrochloride

Dopamine hydrochloride (DH) (10 mM) was prepared by dissolving 0.018 g of it in 0.1M (pH 7.0) phosphate buffer solution (PBS), and the stock solution was stored in a refrigerator at 4°C. This stock solution was diluted to required concentrations as and when required.

Material characterization

The formation of TCP/FC/AuNPs nanocomposite was characterized through Fourier transform infrared spectroscopy (FTIR-Burker Tensor-27 spectro-photometer) in the range of 4000 to 400 cm^{-1} with OPUS software. The surface morphology study was done using Thermo fischer, Quattro S field emission scanning electron microscope (FESEM). XRD patterns were recorded on a X'perts High score plus/Pan Analytical, Philips X-ray diffractometer, equipped with Cu Kα monochromatized photon source (40 KeV, 20 mA, λ= 1.5418 nm) operating at 30 KV and 15 mA and scanned at the rate of 1-10º min^{-1} over the range of 10º-80º (2θ).

Electrochemical characterization

The electrochemical behaviour of TCP, TCP/FC and TCP/FC/AuNPs modified GCE was investigated with the PGSTAT – 12 (Eco chemie, B.V., The Netherlands) Potentiostat/Galvanostat (AUTOLAB) controlled by General Purpose Electrochemical System (GPES 4.9) software. Detection of dopamine hydrochloride was carried out with different pH solutions of phosphate buffered saline (PBS) through cyclic voltammetry (CV), differential pulse voltammetry (DPV) and square wave voltammetry (SWV) with a three electrode setup viz., silver electrode as the reference, platinum wire as the counter electrode and GCE modified TCP/FC/AuNPs as the working electrode.

Catalytic activity of GCE-TCP/FC/AuNPs for electrochemical oxidation of dopamine hydrochloride

Effect of pH

Phosphate buffered saline (PBS 0.1 M buffer solution) was prepared from pH 5.8 to 8.0 to study the effect of pH on GCE-TCP/FC/AuNPs.

Results and Discussion

FESEM analysis

The FESEM images, Fig. 1A, showed a layered sheet like structure for TCP. The SEM image of ferrocene and TCP as shown in Fig. 1B confirms the large surface modification. The AuNPs on TCP/FC are clearly evident in Fig. 1C.

XRD studies

A strong and broad diffraction peak at 16.5°(2θ) for TCP could be due to (001) [Fig. 2A(i)] The peak at

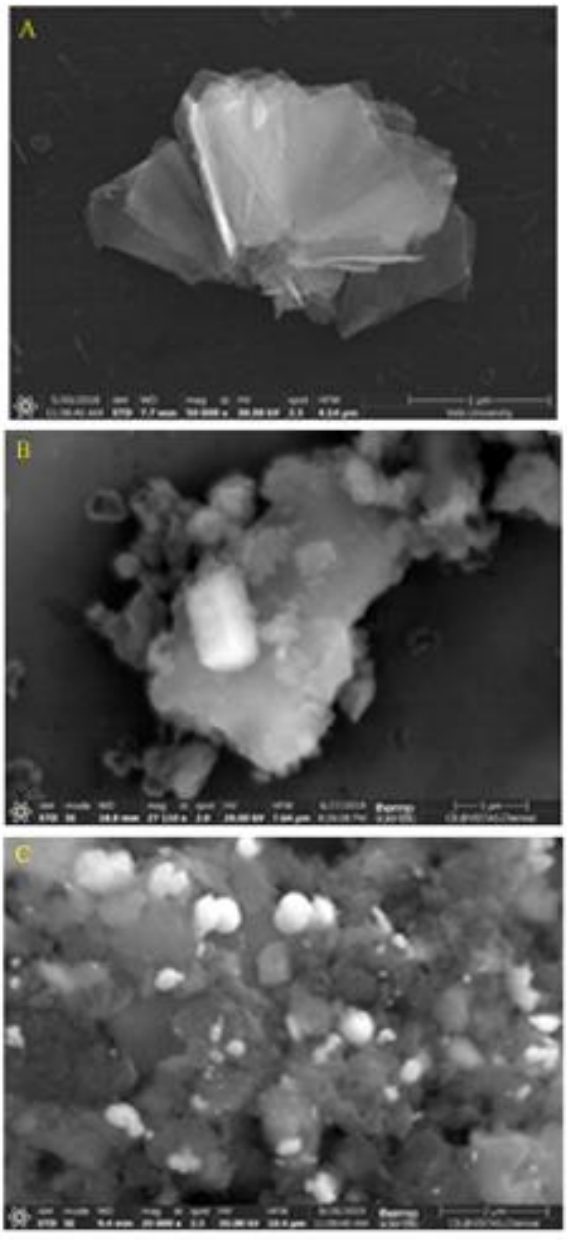


Fig. 1 — FESEM images of (A) TCP (B) TCP/FC and (C) TCP/FC/AuNPs

22.4° (002) is assigned to the aromatic carbon sheets. Decoration of FC on TCP exhibited sharp peaks at 15.38°, 17.26°, 18.37°,19.12°, 19.73°, 22.87°,[38] 25.5°, and 26.9° (2θ), due to (110), (001), (200), (201), (111), (211), (210) and (120), respectively [Fig. 2A(ii)]. Gold (Au) nanoparticle loaded TCP/FC showed the characteristic peaks at 26.5°, 43.2°, 64.5° and 77.6° (2θ) due to (111), (200), (220) and (311), respectively [Fig. 2A(iii)]. In addition, the peak positions reveal shifting of angular reflections to higher angle due to AuNPs addition.

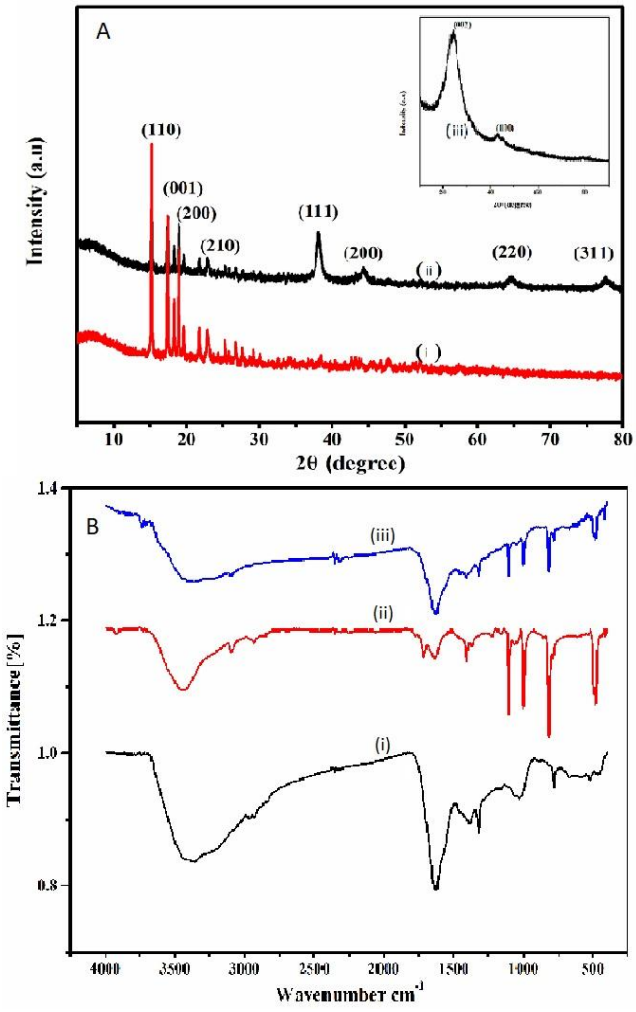


Fig. 2 — (A) X-ray diffraction patterns and (B) FT-IR spectra of (i) TCP (ii) TCP/FC (iii) TCP/FC/AuNPs

FTIR analysis

The FTIR spectra of TCP showed N – H and –OH stretching vibrations around 3353.7 cm^{-1} [Fig. 2B(i)]. The peaks occurred just below 3000 cm^{-1} are due to symmetric and asymmetric stretching vibrations of $–CH_2$- groups, but they are not clearly resolved due to broadening. Ferrocene does not have strong and characteristic IR or Raman bands[39]. The most significant bands (811, 1002, 1108, 1411, 3085 cm^{-1}) overlap with the broad and intense bands of activated carbon around 1314, 1625 and 3095 cm^{-1} [Fig. 2B(ii)]. This broadening is due to the modification of TCP with FC. The N-H and –OH stretching vibrations occurred around 3361 cm^{-1}. The peaks at about 1626 and 1408 cm^{-1} [Fig. 2B(iii)] are due to –COO and $–CH_2$ bending vibrations of GO.

The alcoholic C–O stretching around 1050 cm^{-1} is not clearly resolved due to broadening of ferrocene bands.

Catalytic activity of GCE-TCP/FC/AuNPs

Effect of pH

The effect of pH on GCE-TCP/FC/AuNPs on the detection of dopamine and is shown in Fig. 3. It was observed that there was no significant current response of DH in pH <5 and >7.6. The oxidation potential of DH increased linearly with the increase in pH of the PBS solution (pH 5.8 to 8.0). At the pH 7.0, GCE-TCP/FC/AuNPs showed high current of 14.3 × 10^{-5} A at low peak potential of 0.23 V which suggests the optimum pH 7 for the working electrode. The Nernstian slope of -53 $mVpH^{-1}$ for GCE-TCP/FC/AuNPs confirms the redox reaction of DH

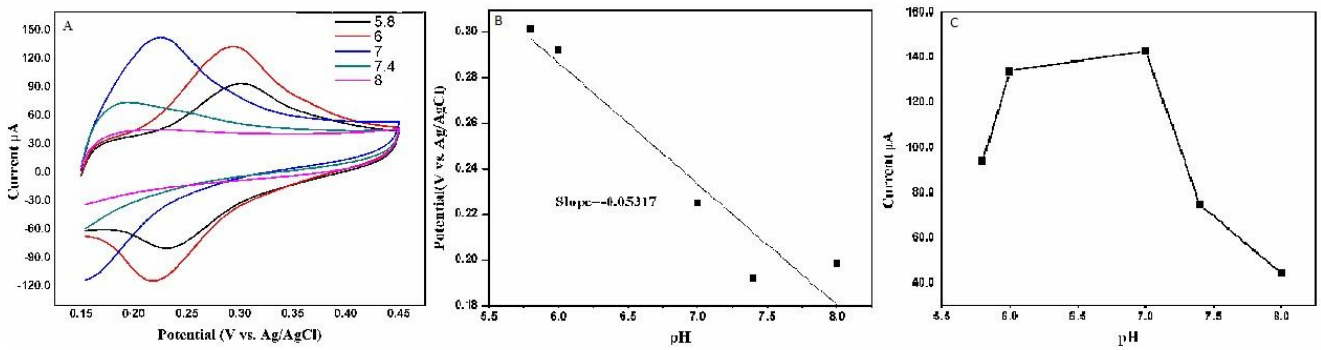


Fig. 3 — Effect of pH on the oxidation of DH in PBS (pH 7.0) at GCE-TCP/FC/AuNPs at different pH

proceed through an equal number of proton and electron transfer. The anodic peak potential was shifted to the negative value with the increase in pH. The plot for Epa *vs*. pH in 0.1 M PBS yielded a linear regression equation

$E^{o}_{1/2}$ = -53 + 0.0589 (correlation coefficient γ =0.8949) …(1)

The mechanism for oxidation of dopamine hydrochloride is proposed in the following reaction Scheme 2.

Effect of scan rate

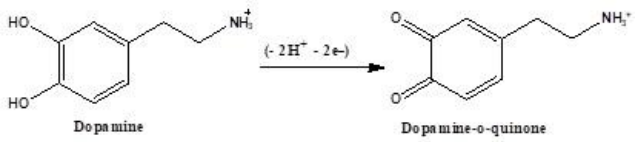
The cyclic voltammograms for the effect of scan rate on the peak current of DH obtained for TCP/FC/AuNPs modified GC electrode is shown in Fig. 4A. The Scan rate varying from 5 to 700 mVs^{-1} was employed for GCE-TCP/ FC/AuNPs in 0.1M PBS (pH 7.0) containing 1mM DH. A linear calibration plot in which the anodic and cathodic peak currents were linearly proportional to the scan rate reveals that the process on the modified electrode is adsorption controlled. A plot of square root of scan rate verses current yielded two straight lines with a slope of -7.61×10^{-7} for cathodic peak and 1.05×10^{-6} for anodic peak (Fig. 4B). The adsorption-controlled process is further confirmed by the linear relationship of a double logarithmic plot between scan rate and peak current with a slope value of 0.6773 (Fig. 4C). The linear regression equation for the anodic and cathodic peak currents for DH is given below.

$I_{pa} = 1.05 \times 10^{-6} (v^{1/2}) + 4.3794 \times 10^{-6} (R^2 = 0.9899)$ …(2)

$I_{pc} = -7.61 \times 10^{-7} (v^{1/2}) + 4.1781 \times 10^{-7} (R^2 = 0.9918)$ …(3)

Detection of dopamine hydrochloride

The sensitivity of GCE-TCP, GCE-TCP/FC and GCE-TCP/FC/AuNPs were studied through differential pulse voltammetry. A potential range from 0.15 to 0.35 V was applied. The DPV curves of GCE-TCP obtained for the increase in concentration of DH from 1.99 to 10.55 μM are shown in Fig. 5A. The anodic peak currents showed a linear relationship with the concentration of DH with correlation coefficient of 0.9818. The limit of detection (LOD) and limit of



Scheme 2 — Electrochemical oxidation of dopamine hydrochloride

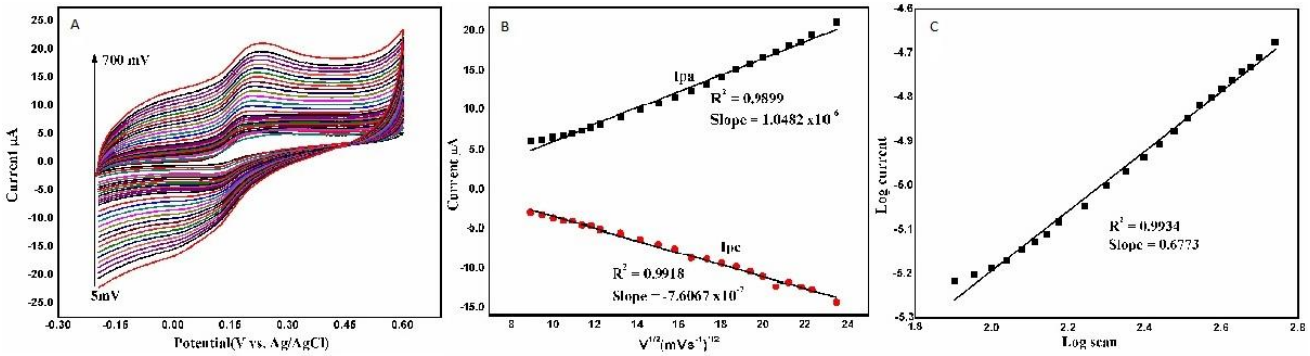


Fig. 4 — (A) Effect of scan rate on oxidation of DH in PBS (pH 7.0) at GCE-TCP/FC/AuNPs at different scan rates, (B) Plot of oxidation peak current *vs*. square root of scan rates and (C) Double logarithmic plot of log *v vs*. log ip

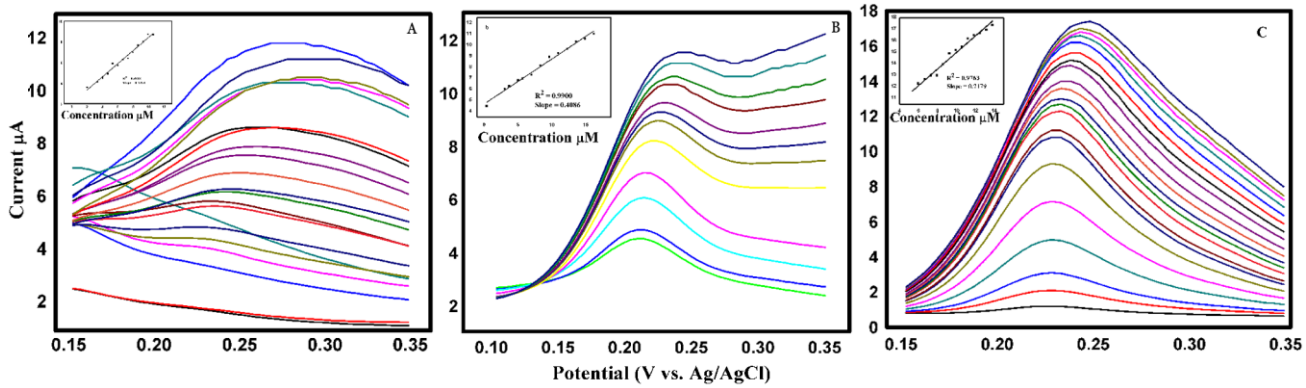


Fig. 5 — DPV of oxidation of DH in 0.1M PBS with (A) GCE-TCP (B) GCE-TCP/FC and (C) GCE-TCP/FC/AuNPs at different concentrations of DH in 0.1 M PBS at a scan rate of $50mVs^{-1}$ (Inset: Calibration plot for concentration of DH *vs*. Current)

quantification (LOQ) were equal to 3.51 and 11.7 μM, respectively with a sensitivity of 0.741 μAμM^{-1}. The DPV curves obtained for the increase in concentration of DH from 0.66 to 16.47 μM are shown in Fig. 5B. The anodic peak currents showed a linear relationship with the concentration of DH with correlation coefficient of 0.9900.

The LOD and LOQ were equal to 3.34 and 11.1 μM, respectively with a sensitivity of 0.45 μAμM^{-1}. The DPV curves obtained for the increase in concentration of DH from 5.96 to 13.8 μM is shown in Fig. 5C. The anodic peak currents showed a linear relationship with the concentration of DH with correlation coefficient of R^2 = 0.9919. The LOD and LOQ) were equal to 2.99 and 9.95 μM, respectively with a sensitivity of 1.36 μAμM^{-1}. Compared to GCE-TCP and TCP/FC control electrodes, the GCE-TCP/FC/AuNPs showed a low detection limit and high sensitivity. The stability of the GCE-TCP/FC/AuNPs was observed by differential pulse voltammetry through 50 repetitive measurements of the oxidation peak current for a time interval of 5 min. Thus, the stability of the modified electrode is confirmed through the retention of 98% of its initial oxidation peak current. The detection limit is calculated using the equation

Detection Limit = 3 × s/m[40].

Case I

Calculation of LOD and LOQ

LOD = 3 × s/m; LOQ = 10 × s/m

Where, s = standard deviation and m = slope of the calibration graph

s = 1.36 μAμmol^{-1}; m = 1.3716

LOD = 2.99 μM and LOQ = 9.95 Mm

Conclusions

In the present work, a novel inexpensive, stable and electrochemically active nanocomposite was prepared by a simple grinding technique using TCP derived from onion petals, ferrocene (FC) and AuNPs. Further, this electrochemically active nanocomposite was used to modify the surface of glassy carbon electrode and thus fabricated GCE-TCP/FC/AuNPs electrode. In the electrochemical analysis, this electrochemical sensor exhibits excellent electrocatalytic activity towards the oxidation of dopamine hydrochloride at pH 7. The oxidation was a two-electron transfer process. The linear relationship between the scan rate and the peak current proves that the reaction occurs through adsorption-controlled process which is confirmed by the slope value of 0.6566. Furthermore, the electrode exhibited high stability, sensitivity, selectivity and reproducibility. It has been found that the modified electrode detects the dopamine hydrochloride (DH) for a wide range of concentration from 5.96 × 10^{-6} to 0.1 × 10^{-4} M. The limit of detection and limit of quantification of the electrode were 2.99 × 10^{-6} and 9.95 × 10^{-6} M, respectively. Further, it is concluded that we have developed simple and effective electro chemical sensor which can be extended for the detection of various other biomolecules at low concentrations under specific physiological conditions.

Acknowledgement

This work was financially supported by University of Madras, India, under University Research Fellowship (URF) scheme.

Conflict of interest

The authors declare no conflict of interests in this study.

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