An approach to widen the electrochemical sensor on dopamine based on the electrode of a MWCNT/RTIL/CrHCF composite

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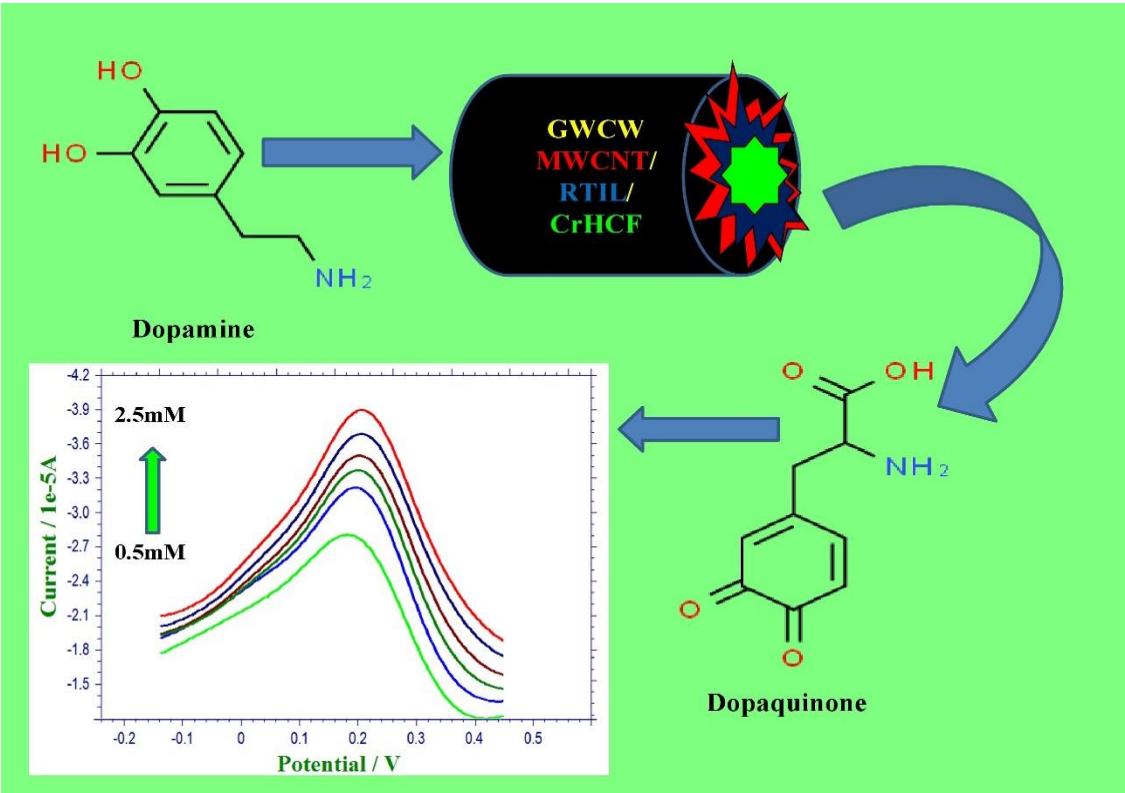
Abstract
The unique properties of carbon nanotubes make it very attractive for amperometric sensors. The rapid development of new nanomaterials and nanotechnology has opened up many opportunities for electrical analysis. Modification of the electrode surface by transferring mechanical modifiers is a new field that requires extensive research. This study demonstrates the expansion of electrochemical sensors based on MWCNT/RTIL/CrHCF nano composites (MWCNT/RTIL/CrHCF) modified with graphite electrodes for the detection of dopamine (DP) at 0.1 KNO_3. (pH 7). The modified graphite composite electrode (GCE) is equipped with an appropriate amount of chromium deposited on the surface of MWCNT/RTIL/GCE and then hexacyanoferrate (CrHCF) is electrodeposited. Ultraviolet visible radiation, HR TEM, XRD, FTIR, EIS and CV (cyclic voltammetry) were used to examine the morphology and interface characteristics of the composite material. The modified electrode has excellent partial discharge detection performance with a linear range of 0.1 µM to 4.0 µM and a detection limit of 0.0121 nm (signal-to-noise ratio = 3). Under the best conditions, the sensor shows excellent stability and the results are satisfactory while analysing real samples.

Keywords: MWCNT/RTIL/CrHCF electrode, nanocomposite, dopamine, voltammetry, carbon nanotubes.

Introduction

Carbon nanotubes have become a promising building block for the nano-production of electronic devices and sensors due to their excellent physical and electrical properties (such as high tensile strength and high strength). Performance and chemical stability have aroused great interest in application in nano-scale materials science such as hydrogen storage batteries[7,21], super capacitors[13], low-emission electrodes[1] in lithium batteries[1] electrochemical sensors[14,18,24-28] and electrical analysis[2].



Graphical Abstract

However, most studies involve the anode and cathode behaviour of nanotube electrodes[5,6,20]. Depending on the diameter of the tube and the symmetry of the two-dimensional carbon lattice, the electrical behaviour of CNTs is similar to that of metals or micro conductors. In addition, carbon nanotubes have been proven to be better than carbon nanotubes. Carbon nanotubes also exhibit electrocatalytic activity against H_2O_2, NADH, ascorbic acid, dopamine, dopamine and homo cysteine[29,33,34].

The electrocatalytic reaction observed in carbon nanotubes has attracted people's attention and this effect can be explained by the presence of the inner edge plane of the wall and the graphite region at the end of the carbon nanotube. The good catalytic activity of carbon nanotubes on these molecules has opened the way for their application in the development of amperometric sensors.

The ionic liquid: Ionic liquid is a kind of salt, in which the coordination of ions is very poor, making these solvents liquid at temperatures below 100°C and even at room temperature (ionic liquid at room temperature, RTIL)[15]. One ion has a delocalized charge, while the other component is an organic ion. It prevents the formation of a constant crystal lattice. Methyl imidazolium and pyridinium ions have proven to be good starting points for the development of ionic liquids. 3,4-Dihydroxyphenylethylamine is an important neurotransmitter in the central nervous system of mammals (CNS) and its electrical activity can be detected electrochemically. The electrochemical oxidation of dopamine is mainly carried out on the carbon electrode [10]. Parkinson's disease (PD) is a neurodegenerative disease that gradually damages the extra pyramidal system and regulates the communication between neurons in the brain and human muscles.

Cells cause dopamine deficiency which in turn leads to violation of the blood-brain barrier. When basic exercise methods (such as reaching, typing, walking, objects and other basic procedures) do not work properly, dopamine deficiency can be overcome[6,8].

In this study, we explained the unique properties of carbon nanotubes, which are very attractive for amperometric sensors. The rapid development of new nanomaterials and nanotechnology provides many opportunities for electronic analysis. The MWCNT / RTIL / CrHCF modified electrode also has high sensitivity for the detection of dopamine.

Material and Methods

Dopamine, a reagent purchased from Himedia (P) Ltd, India, MWCNT and $K_4[Fe(CN)_6]$ purchased from Merck (Mumbai, India) were used in electrochemical technology. Ionic liquid 1-ethyl, 3-methylimidazolium, hexafluoro phosphate, potassium ferrocyanide (0.02 M) and KNO_3 (0.1 M) as electrolyte are used to coordinate the Fe ions of hexacyanoferrate by derivatization.

Preparation of Wax Impregnated Electrode: Immerse it in molten paraffin (molecular weight: 70°C to 80°C) and keep it under vacuum until there are no more bubbles. Remove the rod before the wax hardens. The electrode is polished with polishing paper and rinsed thoroughly before use.

The cleaning of multilayer nanotubes: Cleaning of functionalized CNT is important step in the production of functionalized nanotubes. In a typical experiment, ultrasonic treatment is used for 30 minutes in advance and then the MWCNT is washed in concentrated HCl, then stirred for a long time, centrifuged, filtered and thoroughly washed with double distilled water. Heat to 225°C. The heat treatment was repeated at 325°C for 1.5 hours and at 350°C for 1 hour and then sonicated in concentrated HCl. It was exposed to 12.8M nitric acid and refluxed for 12 hours, washed with water and dried. It is known that this treatment causes the cleavage of MWCNTs and the formation of -COOH groups on its ends and sidewalls.

MWCNT is mixed with ionic liquid and then fixed. Coat on the WIGE graphite electrode and let it dry. Immerse the dried electrode in a solution containing 0.1 M KNO_3 to obtain 1 M potassium hexacyanoferrate. Let it stand overnight, then remove it from the solution and dry it.

Results and Discussion

Morphology of the nanoparticles

TEM analysis of MWCNT/RTIL/CRHCF hybrid: The TEM can be used to examine the RTIL morphology and distribution on the surface of the functionalized carrier of MWCNT. Fig. 1 (a and b) shows typical electron microscope images of RTIL-modified MWCNT surfaces. It can be seen that the average size of CNTs is 12 nm widely distributed in MWCNT in the large coating CNT conjugated probe. This prevents biomolecules from escaping from the composite membrane and improves the stability of the sensor[11,31]. This interesting phenomenon will be very useful in practical applications such as biosensors.

Optical absorption: The combination of RTIL and functionalized MWCNT/CrHCF surface was further confirmed by ultraviolet-visible spectroscopy. Figure 2 shows the typical light absorption spectrum of MWCNT/RTIL/CrHCF hybrid. The strong absorption at 520 nm respectively was attributed to Plasmon resonance of essentially isolated RTIL adsorbed onto MWCNTs (i.e. the hybrid material).

XRD analysis of MWCNT/RTIL/CRHCF hybrid: Figure 3 shows the obtained X-ray diffraction pattern of the MWCNT/R1TIL/CrHCF hybrid. MCNT shows typical peaks of CNT or graphite (002) phase[32] and the peaks appear at 38.3°, 44.5°, 64.7°, 77°. The diffraction peaks of iron crystals (111), (200), (220) and (311) are designated as 7° and 81.8° respectively which are consistent with the results of the TEM image.

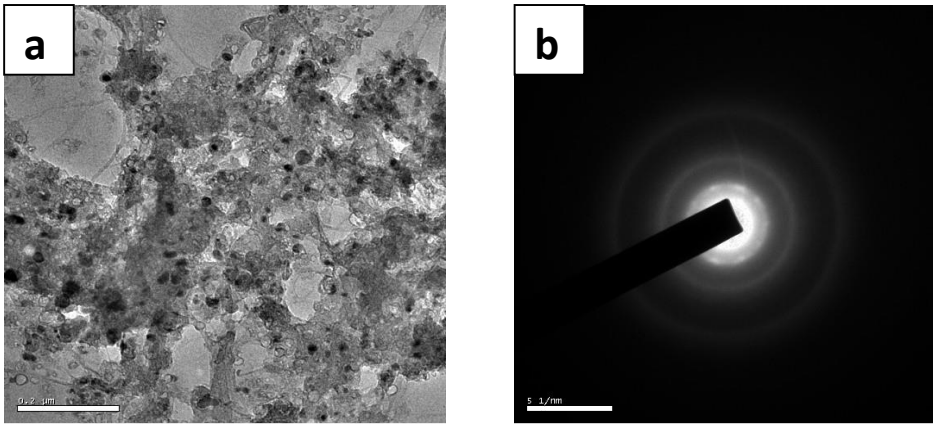


Figure 1: TEM analysis of MWCNT/RTIL/CrHCF hybrid

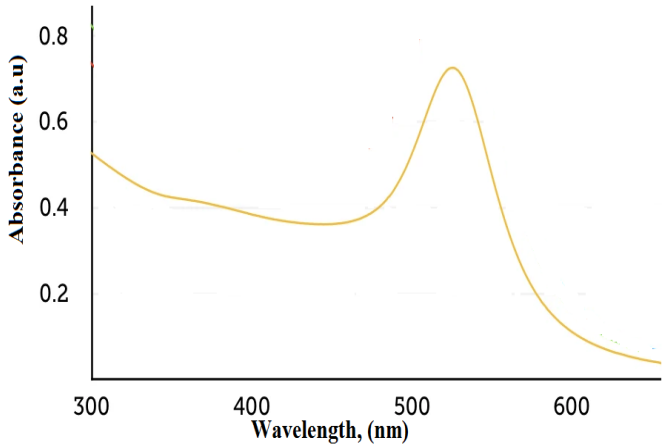


Figure 2: Optical absorption of Modified Electrode

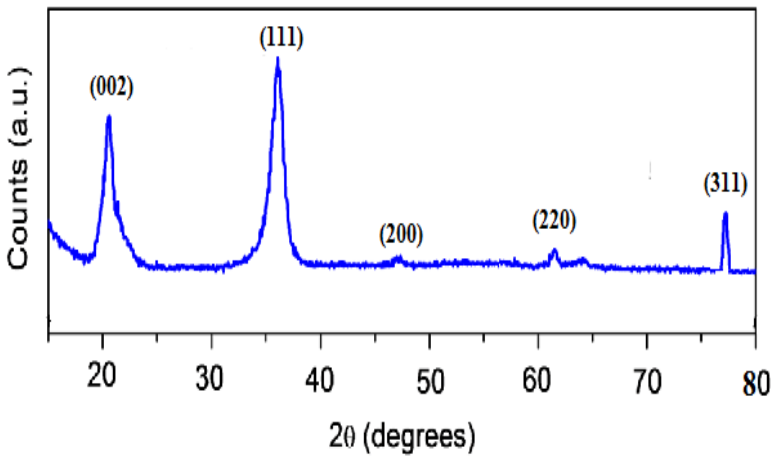


Figure 3: XRD analysis of MWCNT/RTIL/CrHCF hybrid

FTIR analysis of MWCNT/RTIL/CrHCF: The FTIR spectrum of the chromium hexacyanoferrate nanoparticles (Figure 4) shows the absorption spectrum where the charge transfer shoulder from Fe ^{II} to Fe ^{III} is in the range of 530-550 nm and there is a broad band around 390 nm, which was previously determined. In the transition[23] from Fe^{II} to Fe^{III}, broad mountain peaks appear in the area from 2050 to 2090 cm^{-1} and above and from 2120 to 2130 cm $^{-1}$ which can be assigned to ν (CN) Fe^{II}-CN-Fe^{III} (reduced form) and Fe^{II}-CN-Fe^{III}[22]. ν(N-H) can also be identified at 1499 cm^{-1}.

Cyclic voltammetric studies of the modified electrode: The modified electrode and barometer electrode were used as working electrodes and 0.1 M KNO_3 solution was used as the supporting electrolyte to scan the potential from -0.2 V to 0.6 V·s SCE. The potential is sampled at 20 mV/s and the resulting cyclic voltammogram is shown in fig. 5. This figure shows that compared to ERS, the modified electrode shows a well-defined reversible redox peak where the anode peak is at 0.2 V and the cathode peak is at 0.18 V. This reversible reaction is explained by an electron transfer

reaction involving $[Fe(CN)_6]^{4-}/[Fe(CN)_6]^{3-}$ pairs, which are present on the electrode surface and in contact with the background electrolyte. The incomplete behaviour of the electrode explains the following reasons:

- Repulsive interactions between ions in the crystal lattice.
- The difference in the spatial distribution of redox centres.
- Distribution of particles with different Eo importance.

Effect of Supporting Electrolytes: The type of electrolyte has a significant effect on the volt-ampere characteristics of the mediator fixed on the electrode. At a sampling rate of 20 MV/s, CV was recorded in 0.1 M solutions of various electrolytes such as NaCl, NH_4Cl, $Ca(NO_3)_2$, K_2SO_4 and KNO_3.

In all these electrolytes, a well-defined cyclic voltammogram can only be obtained in the presence of 0.1 M KNO_3 solution.

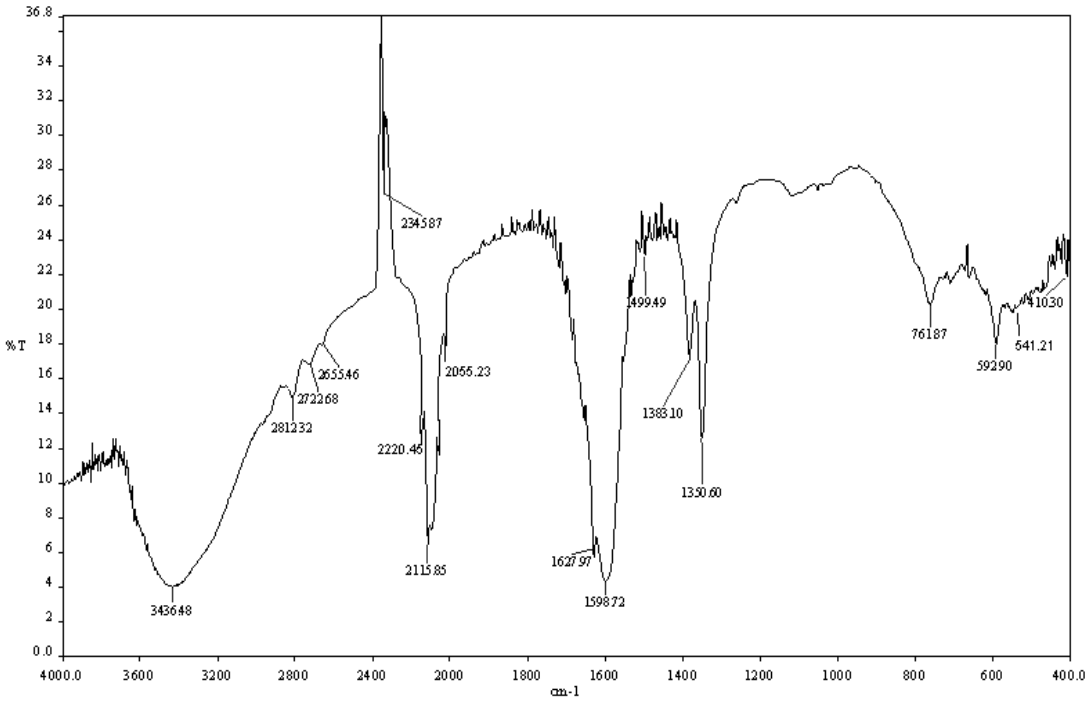


Figure 4: FTIR analysis of MWCNT/RTIL/CrHCF

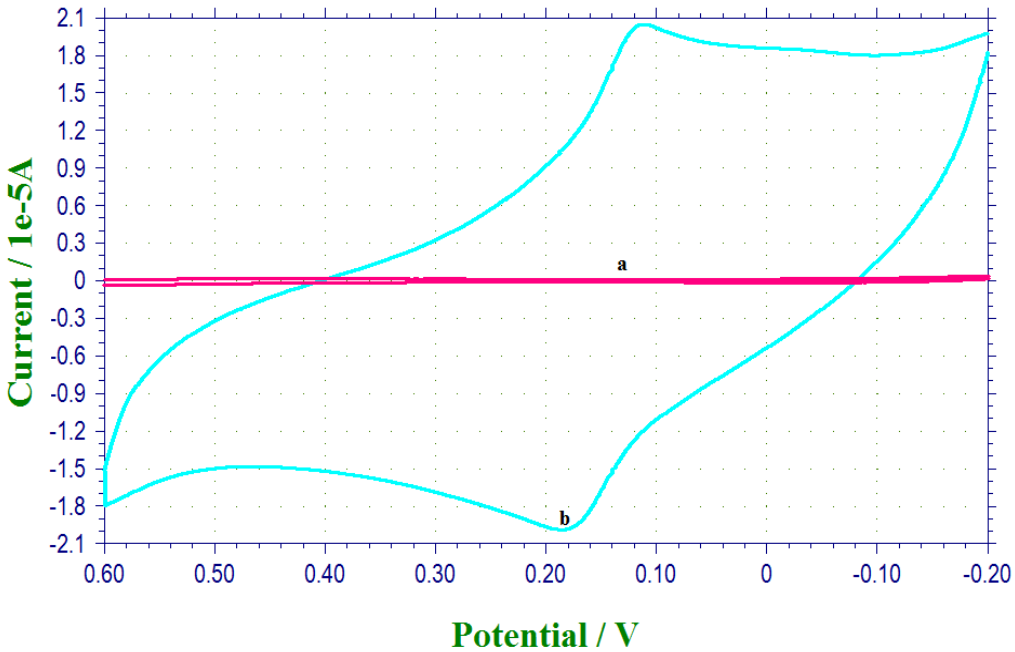


Figure 5: CVs for the (a) Bare WIGE and (b) MWCNT/ RTIL/CrHCF modified electrode; Electrolyte: 0.1M KNO_3 Scan rate: 20mVs^{-1}

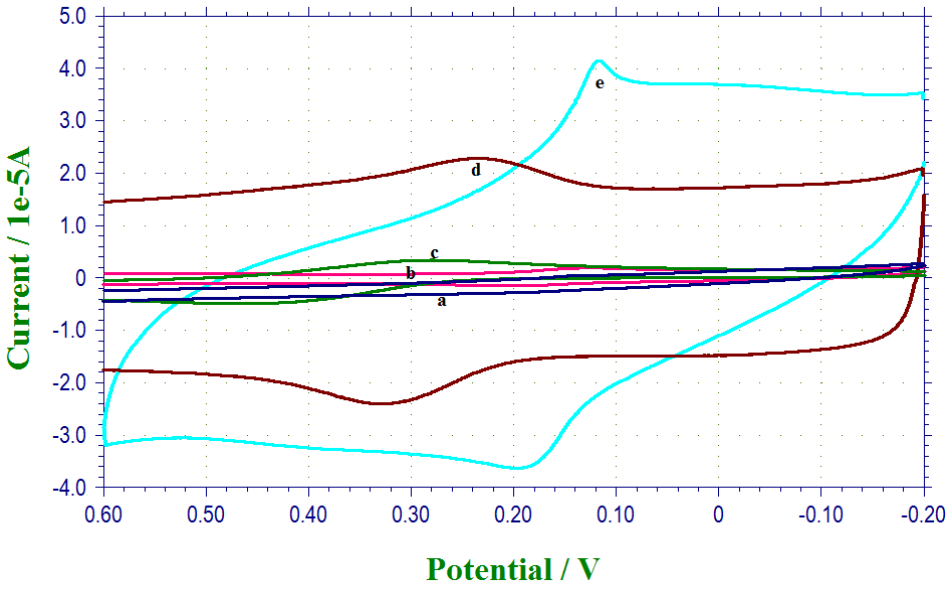


Figure 6: CV for MWCNT/RTIL/CrHCF modified electrode in 0.1M solution of (a) $CaCl_2$ (b) NaCl (c) NH_4Cl (d) KCl, (e) KNO_3 Scan rate: 20mVs^{-1}

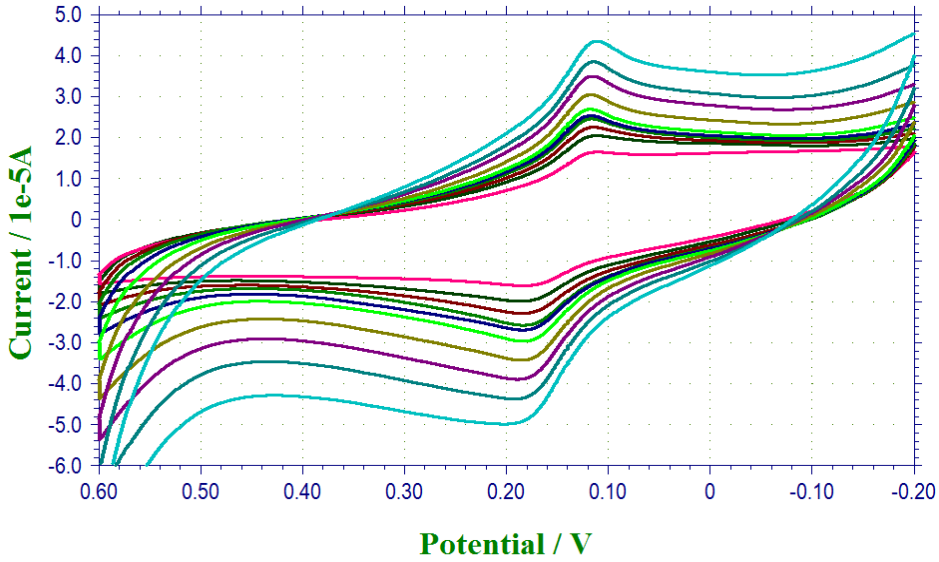


Figure 7: Cyclic voltammogram for MWCNT/RTIL/CrHCF modified electrode with increase in potential scan rate for (a-j)10-100 mVs^{-1} in 0.1M KNO_3

Effect of Scan Rate Variation: In order to study the influence of scan rate on the reaction of modified electrode with MWCNT/RTIL/ferrocyanide, cyclic voltammograms of modified electrode at different scan rates ranging from 10 mV/s to 100 mV/s were recorded. In figure 7, it can be seen that as the scanning speed increases, the distance between the needle tip and the needle tip also increases. At lower sampling rates, the spacing between peaks is smaller, indicating that electrons and counter ions are transported faster than potential sampling.

Effect of pH: The pH of the solution is an important factor affecting the response of the electrode. By changing the pH value of the supporting electrolyte solution from 2 to 9, the effect of pH on the electrochemical behaviour of the modified electrode was studied. The result is shown in figure 8. pH 7 was the followed for further swot.

EIS - Electrochemical impedance spectroscopy studies: Electrochemical impedance spectroscopy (EIS) is producing an intended result for probing the features of a surface-confined species. EIS was employed to carry out the charge transfer behavior at the modified and bare electrode. Scan the electrode between a range of 1Hz to 0.1M Hz. The activity of the modified electrode at various potentials neighboring the oxidation potential of the redox peaks was studied. The complex plane spectrum was found to fit with a Randles circuit. The constant phase element (CPE) equivalent circuit model (Figure 9. inset circuit) is one in which the double layer capacitance is replaced by the CPE

in Randles' model i.e. Rs(CPE [RctZw]) where Rs is the solution resistance, Rct is the charge-transfer resistance and Zw is the Warburg impedance sufficient to explain the EIS data obtained in this work. The Nyquist plots exhibited the characteristics semicircles (less pronounced for the bare than the modified GCE) at high frequencies and a straight line at low frequencies, corresponding to kinetic and diffusion processes respectively.

As seen in figure 9, the EIS data of the modified electrode at different potentials around the formal potential of the redox peak were recorded. It was seen that the modified electrode offered the least resistance to charge transfer (R_{ct}) when the potential was fixed at the formal potential (E^o) while at the either side, the resistance was comparatively higher. These EIS data (Rs, Rct, CPE and Zw) were extracted from the Nyquist plots. For the bare electrode, the Rs, Rct, CPE and Zwvalues were estimated as 108.2 $k\Omega cm^{-2}$, 29.3 $k\Omega cm^{-2}$, 5.6 $nFcm^{-2}$ and 1.2x$10^{-4}\Omega cm^{-2}s^{1/2}$ respectively. For the CrHCF modified electrode, values of 94.6 $k\Omega cm^{-2}$, 38.54 $k\Omega cm^{-2}$ and 11.2 $nFcm^{-2}$and 7.96 x$10^{-4}\Omega cm^{-2}s^{1/2}$were obtained for the Rs, Rct, CPE and Zw respectively. The Rct value for the modified electrode is less compared to bare GWCE, which indicates that the CrHCF facilitates the electron transfer process and forms a tunable kinetic barrier to the transfer of electrons.

Determination of Dopamine: Take known concentration of dopamine (1.33x10^{-7}M) and conduct electrocatalytic oxidation. The oxidation current is measured by changing the concentration of dopamine. The anodic current generated by the catalytic oxidation of dopamine increases linearly with the indicated dopamine addition. In figure 10, this is observed in the presence of modifiers on the electrode surface. The anode current increases in proportion to the increase in dopamine and shows a linear relationship within this value range.

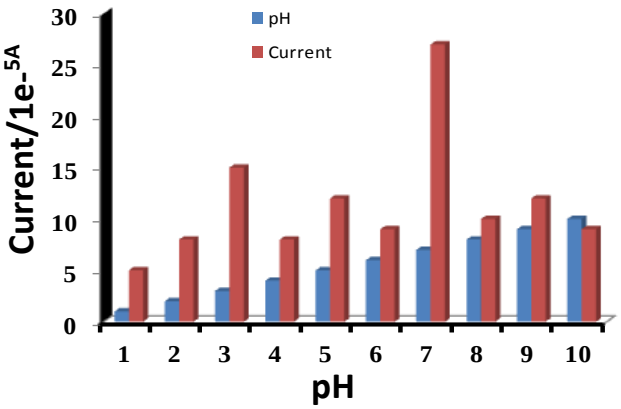


Figure 8: Cyclic voltammograms of pH for MWCNT/RTIL/CrHCF modified electrode.

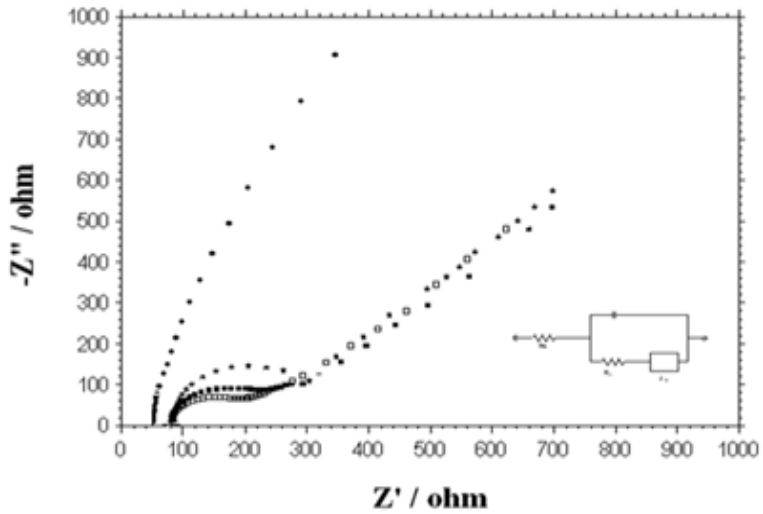


Figure 9: Complex impedance plots of the CrHCF film modified electrode in 0.1 M KNO_3 showing the Nyquist plot obtained for the electrode at the three different potentials (⋆ -200mV), (□-240mV), (▪-300mV) and bare electrode (bare-•) (That means graphite wax composite electrode).
Inset: modified electrode Randels equivalent circuit diagram

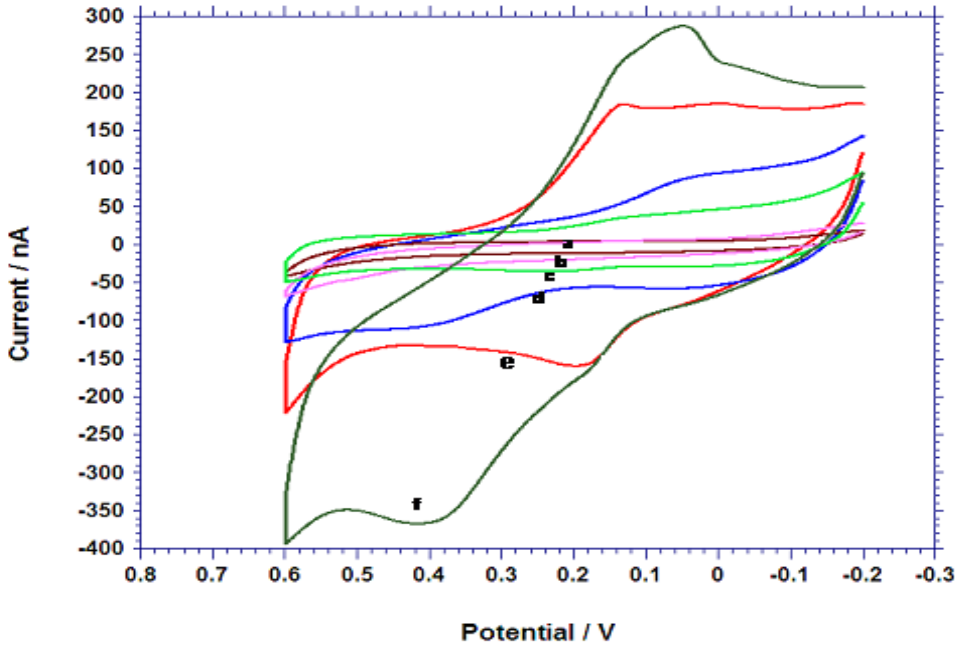


Figure 10: Cyclic voltammograms of (a) bare electrode, (b) 1.33 x 10^{-7}M of dopamine at bare electrode. (c) MWCNT/RTIL, (d) 1.33 x 10^{-7}M of dopamine at MWCNT/RTIL electrode, (e) MWCNT/RTIL/CrHCF (f) 1.33 x 10^{-7}M of dopamine at MWCNT/RTIL/CrHCF modified electrode. Scan rate:20mVs^{-1}

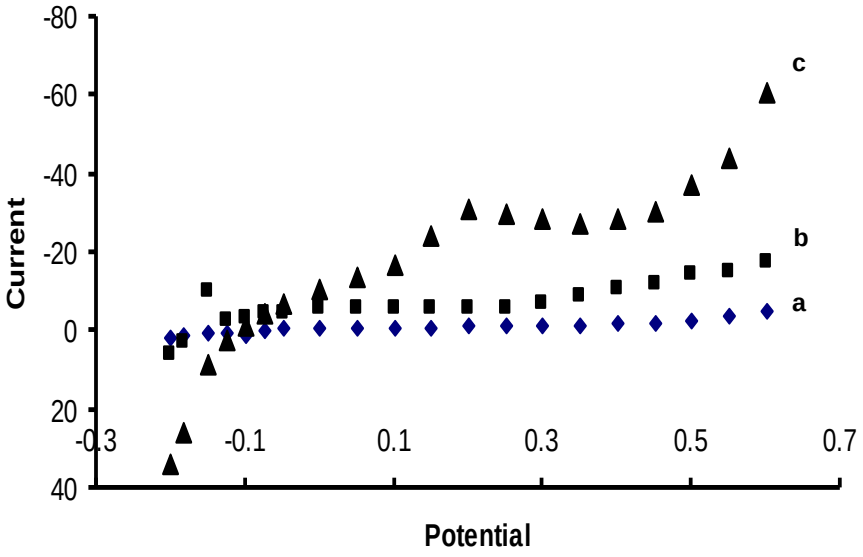


Figure 11: Hydrodynamic voltammograms in 0.1M KNO_3solution for (a) bare (b) MWCNT/RTIL (c) MWCNT/RTIL/CrHCF modified electrode with 1.33 x 10^{-7}M dopamine. Stirring rate: 300 rpm.

Hydrodynamic Voltammetry: The fluid dynamic voltammetry of catalytic oxidation for catalysis studies was carried out using improved electrodes in a flow system. Figure 11 shows that HDV is obtained by bare electrode (curve a), MWCNT/RTIL electrode (curve b) or MWCNT/RTIL/CrHCF (curve c).

It can be seen that the curve in the modified electrode improves the current response to dopamine oxidation obtained at a reduced potential. However, for un insulated electrodes, the response to dopamine oxidation at low potentials is poor. Dopamine oxidation was observed. The stable volt-ampere characteristics under stirring conditions show its applicability in flow systems.

Chronoamperometry: Figure 12 shows the ampere response in the modified MWCNT / RTIL / CrHCF electrode when 1×10^{-4} M dopamine is continuously added each time. A well-defined current response to dopamine is obtained in the improved osmotic sensor. In order to achieve dynamic equilibrium, each time the sample solution is added, the reaction that occurs in the modified electrode is very rapid. The step increment of each step is the same.

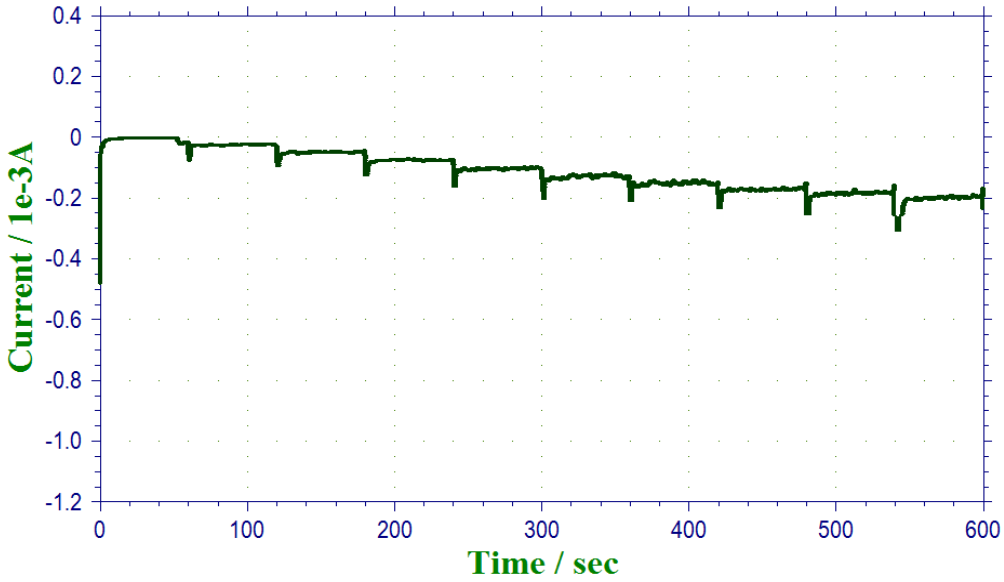


Figure 12: Chronoamperometric response of the MWCNT/RTIL/CrHCF modified electrode with 2.66 x 10^{-5}M of dopamine. Electrolyte: 0.1M KNO_3. Stirring rate: 300 rpm.

Conclusion

The experimental results given above show that this work demonstrates a new method for the production of amperometric sensors based on the functionalization of CNT on the surface and the anchoring of mediators. The sensor is manufactured by mechanically fixing the functionalized CNTs on the surface and evacuating them at room temperature. An anion exchange between the hexacyanoferrate and the ionic liquid was carried out at the same time. The cyclic voltammogram showed that the modified MWCNT / RTIL / CrHCF electrode showed a reversible peak in E0 of 0.10 V and a reversible peak in SCE of 0.1 M KNO_3.

The reversible peak corresponds to the redox reaction of the mediator. It is linearly proportional to the square root. Suppose the redox reaction is controlled by the diffusion sampling rate. The electrochemical behaviour of modified electrodes and electrolytes with different cations and anions shows that the cyclic voltammogram depends on the electrolyte environment. The electrode showed a very stable response over repeated cycling (almost 100 cycles). The results show that the method is simple and easy to implement. It is a promising and reliable method for determining dopamine.

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