Trends in Sciences
TRENDS IN SCIENCES 2026; 23(3): 11907
DJMP Center for Digital Journal Management & Multidisciplinary Academic Platform
https://doi.org/10.48048/tis.2026.11907
RESEARCH ARTICLE

Screen-Printed Electrodes Modified with Fe_3O_4-Activated Carbon Derived from Spent Coffee Grounds for Dopamine Detection in the Presence of Ascorbic Acid and Uric Acid

Tharaton Nooin[1], Thaneeya Hawiset[2] and Prachak Inkaew[1,*]

[1]*Center of Chemical Innovation for Sustainability, School of Science, Mae Fah Luang University, Chiang Rai 57100, Thailand*
[2]*School of Medicine, Mae Fah Luang University, Chiang Rai 57100, Thailand*

([*]Corresponding author's e-mail: prachak.ink@mfu.ac.th)

Received: 15 September 2025, Revised: 22 September 2025, Accepted: 10 October 2025, Published: 20 December 2025

Abstract

Dopamine, a critical neurotransmitter involved in regulating nervous and immune system responses, is essential for maintaining overall health. Abnormal dopamine levels are linked to neurodegenerative diseases such as Alzheimer's and Parkinson's. Accurate measurement of dopamine, particularly in blood where other interfering substances like uric acid and ascorbic acid are present, is crucial. This study focuses on developing a selective and sensitive electrochemical method for dopamine detection using Fe_3O_4-activated carbon electrodes derived from pyrolyzed spent coffee grounds. The prepared electrodes exhibit enhanced stability and electrocatalytic properties due to the synergistic effects of high surface area, oxygen-containing species, and the catalytic properties of Fe_3O_4. Detailed characterization of the Fe_3O_4-activated carbon composite was conducted using XRD, SEM, FTIR, and cyclic voltammetry, confirming the successful incorporation of Fe_3O_4 and the presence of functional groups essential for redox reactions. The modified electrodes demonstrated significant improvements in dopamine detection, achieving a detection limit of 0.92 µM with a linear range of 1 - 1,325 µM, and effectively minimizing interference from ascorbic acid and uric acid. The practicality of the developed method was validated through successful dopamine detection in a human serum sample, highlighting its potential for real-world applications in clinical diagnostics.

Keywords: Dopamine, Activated carbon, Spent coffee ground, Screen-printed electrode, Magnetic carbon, Square wave voltammetry, Electrochemical analysis, Nafion

Introduction

Dopamine (also known as 3,4-dihydroxyphenylethylamine) is an important neurotransmitter. Dopamine is a neurotransmitter released by the brain to transmit signals to various organs. It is a small molecule belonging to the catecholamine group and can undergo redox reactions. Dopamine plays a crucial role in the functioning of the nervous system, regulating responses to stimuli and various immune systems in the body. It is a substance released by the brain during pleasure. An excessive or insufficient level of dopamine can have implications for the health and functioning of different systems in the body. Well-known diseases resulting from abnormal dopamine levels include Alzheimer's disease and Parkinson's disease. Various methods for dopamine measurement exist, such as liquid chromatography [1-3] , fluorescence spectroscopy [4-6], and surface-enhanced resonance Raman spectroscopy [7-10]. However, the aforementioned methods are costly for analysis and may require long analysis times, or some methods involve large sample volumes. Electrochemical analysis is a viable method for dopamine measurement, utilizing different types of electrodes [11-13]. However, electrochemical analysis for dopamine still faces challenges in terms of low selectivity and interference from other substances present in bodily fluids, such as ascorbic acid and uric acid, which can undergo reactions at the same electric potential as dopamine, leading to overlapping peaks and complicating dopamine analysis. Reports have described the modification of electrodes using carbon dots [14], carbon nanotubes [15-17] graphite [13], graphene [18,20], reduced graphene oxide [21], boron-doped diamond [8,22], DNA [7,23,24], and carbon aerogel [25] for dopamine detection purposes.

The surface functional groups of carbon electrodes can be modified in terms of both the type and quantity of functional groups through additional activation processes. Two common activation methods are electrical activation and acid/base activation [26,27]. Electrical activation involves applying a positive electric potential to the electrode that requires activation in an acidic solution. The electric potential, intensity, and type of acid used during activation influence the quantity and type of oxygen-containing species that are formed [26,28]. Acid/base activation, on the other hand, involves soaking the carbon in an acidic or basic solution to induce activation. The quantity and type of oxygen-containing species formed depend on the type and concentration of the acid or base used [26]. The presence of oxygen-containing species on the electrode surface significantly affects the redox reactions or electron exchange on the electrode surface with dopamine [28]. Having a higher density of oxygen-containing species on the surface also helps to repel negatively charged interfering species from approaching the electrode surface, thereby improving the selectivity of the electrode and reducing interference from other species with negative charges. In general, the pH of the solution is adjusted to determine the concentration of dopamine. This is done by adjusting the pH to make dopamine positively charged and closer to the electrode surface due to the electrostatic attraction, the electrode surface is negatively charged due to the presence of oxygen-containing species. Meanwhile, ascorbic acid and uric acid are negatively charged and do not approach the electrode surface, resulting in reduced interference and facilitating more accurate and easier measurement of dopamine [29].

Magnetite (Fe_3O_4) has been widely used as a catalyst in numerous reactions due to its non-toxicity, ease of recovery, and recyclability. It can effectively convert small organic molecules such as CO_2 [30], alcohols [31], and ammonia [32] into other products. Dopamine, ascorbic acid, and uric acid have distinct functional groups and undergo conversion at different potential. The use of Fe_3O_4 could help distinguish the oxidation peaks of dopamine, ascorbic acid, and uric acid, enhancing their redox responses owing to its catalytic properties. However, Fe_3O_4 is unstable in acidic conditions, making its use as a nanoparticle on electrode surfaces without a stabilizing reagent impractical. In this study, modified Fe_3O_4-activated carbon electrodes were prepared. Carbon is known for its ability to stabilize metallic nanoparticles on its surface, reducing agglomeration and enhancing stability. The carbon used in this study was derived from pyrolyzed spent coffee grounds, typically discarded as waste or sold at low prices. Governments encourage coffee farming in mountainous regions to combat deforestation, as coffee grows best under tree shade, thereby incentivizing farmers to preserve trees. Utilizing spent coffee grounds not only adds value to waste materials but also helps in reducing deforestation. Spent coffee grounds, rich in fat and moisture, undergo carbonization at high temperatures (500 - 800 °C), evaporating fats, organic substances, and water to form porous structures, significantly increasing surface area and enhancing redox reaction responses. The resulting carbon was activated with acid to introduce oxygen-containing species on the surface. Fe_3O_4 was then adsorbed onto the carbon surface, forming a composite of Fe_3O_4-activated carbon.

Nafion is a synthetic polymer that has become a cornerstone material in electrochemistry due to its unique properties. It is a perfluorosulfonated ionomer, which means it has a hydrophobic Teflon backbone with hydrophilic sulfonic acid side chains. This dual structure allows it to self-organize into distinct domains: a rigid, chemically inert scaffold and an interconnected network of hydrophilic channels. In electrochemical analysis, Nafion is widely used as a proton exchange membrane or a permselective coating on electrodes. When used as a coating, the negatively charged sulfonate groups within the Nafion film repel other negatively charged species, such as anionic interferents, while attracting and pre-concentrating positively charged species. This charge-based selectivity is crucial for enhancing the signal-to-noise ratio in sensors for positively charged analytes [33,34]. In electrocatalysis, Nafion serves as an essential ionomer binder in catalyst layers. It connects the catalyst particles to the proton-conducting pathways, ensuring efficient transport of reactants and products to and from the active sites. Nafion's stability in harsh chemical environments and its ability to maintain a humid microenvironment around the catalyst are vital for high-performance applications like proton exchange membrane (PEM) fuel cells and electrolyzers, where it enables efficient proton transport and enhances overall catalytic activity [35]. The synergistic effects of the high surface area, oxygen-containing functional groups, negatively charged Nafion coating, and the electrocatalytic properties of Fe_3O_4 are expected to enhance the signal response and selectivity in dopamine detection.

This study aims to develop a sensitive and selective electrochemical method for detecting dopamine in the presence of interfering substances such as uric acid and ascorbic acid. The research focuses on the use of Fe_3O_4-activated carbon electrodes derived from pyrolyzed spent coffee grounds, which provide enhanced stability and electrocatalytic properties. Detailed characterization techniques, including X-ray diffraction (XRD), scanning electron microscopy (SEM), Fourier-transform infrared spectroscopy (FTIR), and cyclic voltammetry, were employed to assess the material's properties. Additionally, the method was validated using human serum samples, demonstrating its potential for clinical diagnostics and real-world applications.

Materials and methods

Chemicals and instrumentation

Unless specified otherwise, all chemicals used in this study were of analytical grade, and used as received without additional purification. Electrolyte solutions were freshly prepared daily using double-distilled Milli-Q water. Screen-printed electrodes (SPEs) consisting of a 2 mm diameter gold working electrode (electrode area: 0.031 cm^2), a gold counter electrode, and an Ag/AgCl (35%/65%) reference electrode were used. The electrodes were manufactured by BVT Technologies (Czech Republic). Electrochemical analysis was performed using the EmStat3+ (Palmsens, The Netherlands) as the control and measurement unit, with data analyzed using PS Trace 5.9 software.

To prepare the buffer solution, NaH_2PO_4 and Na_2HPO_4 were dissolved in Milli-Q water, and the pH was adjusted with NaOH using a Mettler-Toledo S220 pH/Ion meter.

Human serum samples were obtained from Sigma Aldrich, mixed with acetonitrile (1:1 v/v), and centrifuged at 5,000× g for 10 min at room temperature to separate proteins. The supernatant was filtered using Whatman No.1 filter paper.

Spent coffee grounds were obtained from a local coffee shop, dried in an oven at 60 °C, and finely ground with an electric blender. The resulting powder was filtered using a 125-μm mesh sieve.

In standard samples, dopamine concentration was quantified using square wave voltammetry under specific electrochemical parameters. Measurements were conducted in 0.1 M phosphate buffer at pH 7.4, employing a step potential of 4 mV, an amplitude of 40 mV, and a frequency of 25 Hz.

To prepare these standard samples, ascorbic acid and dopamine were dissolved in the 0.1 M phosphate buffer solution. Uric acid, on the other hand, was dissolved in a 0.1 M NaOH solution and sonicated for 5 min to ensure complete dissolution. After sonication, the uric acid solution was diluted appropriately with 0.1 M phosphate buffer at pH 7.4 to achieve the desired concentration for analysis using square wave voltammetry.

Preparation of carbon from the spent coffee grounds

The spent coffee grounds (100 g) underwent combustion in a tube furnace under oxygen-deficient conditions. Prior to and throughout the entire combustion process, the furnace was purged with nitrogen gas at a flow rate of 2 L/min for 10 min. The combustion occurred at a constant temperature of 600 °C for 90 min. The temperature was gradually raised from room temperature to 600 °C over one hour, resulting in a heating rate of approximately 7.8 °C/min. Once the temperature reached 600 °C, it was maintained for the entire 90-minute duration. Subsequently, the temperature was gradually reduced to room temperature over a period of 2 h. After the furnace had completely cooled down, the sample was carefully removed for further processing.

Preparation of activated carbon from the spent coffee grounds

The carbon obtained from the spent coffee grounds underwent an activation process by immersion in 98% sulfuric acid for 24 h. Following this, it underwent several rinses with distilled water and was filtered using filter paper. The resulting carbon was then dried at 70 °C in an oven and stored in a glass container for future use.

Preparation of magnetic activated carbon (Fe_3O_4-activated carbon)

The synthesis of magnetic carbon involves using ferric chloride ($FeCl_3$) and ferrous sulfate ($FeSO_4$) as precursors to introduce iron ions into the carbon structure. Initially, 0.50 g of activated carbon from spent coffee grounds was mixed with a 10 mL solution containing 2.0 g each of $FeCl_3$ and $FeSO_4$. The mixture was stirred for 30 min. Subsequently, 4 M NaOH was added until reaching a pH of 12, and the mixture was heated and stirred for 1 h 60 ℃. Afterward, the mixture was filtered through Whatman No. 1 filter paper and the filtrate was dried in an oven at 80 ℃ for 2 h. The dried product underwent magnetic separation using a strong magnet to isolate Fe_3O_4 from nonmagnetic carbon powder.

Preparation of a Nafion coated screen-printed electrode with Fe_3O_4-activated carbon (Nafion-coated SPE-Fe_3O_4-activated carbon)

The 50 mg of Fe_3O_4-activated carbon composite was mixed with 0.1 mL of Nafion solution (5% Nafion in methanol). Subsequently, a 5 µL aliquot of the resulting mixture was carefully deposited onto the center of a gold electrode on the screen-printed electrode and left to air dry at room temperature. A 5 µL aliquot of the Nafion mixture was selected, as it provides sufficient volume to form a uniform coating on the surface of the screen-printed electrode upon air-drying.

Characterizations of the Fe_3O_4-activated carbon

The morphology of the carbon derived from spent coffee grounds was examined using a field emission scanning electron microscope (FE-SEM, Tescan Mira 4). The surface functional groups present in the carbon were analyzed using a Nicolet iS50 Fourier transform infrared spectrometer (FTIR, Thermo Scientific) equipped with a silicon nitride light source and a deuterated L-alanine triglycine sulfate (DLaTGS) detector. FTIR spectra were acquired with a resolution of 3 cm^{-1}.

X-ray diffraction (XRD) analysis was performed using a PANalytical X'Pert Pro MPD X-ray diffraction analyzer (United Kingdom). The samples were mounted in a holder and scanned from 5.0° to 100.0° at a scan speed of 0.050640 °/s.

Electrochemical characterization of the Nafion-coated SPE-Fe_3O_4-activated carbon

Cyclic voltammetry was performed using a 0.1 M KCl electrolyte solution containing 10 mM $Ru(NH_3)_6Cl_3$ to assess electron transfer ability on the electrode surface. To evaluate this ability, the potential difference between the peak potentials of oxidation and reduction reactions was measured. This difference was compared with the theoretical value of 59 mV, a standard for efficient electron transfer. By comparing experimental and theoretical values, valuable insights into electron transfer efficiency, electrode surface charge nature, and quantity of charges involved in reactions can be obtained. Such insights are crucial for understanding the electrochemical behavior of the system and provide essential data for various applications and analyses.

Results and discussion

Characterizations of Fe_3O_4-activated carbon

Figures 1(A) and **1(B)** show the XRD patterns of activated carbon and Fe_3O_4-activated carbon, respectively. The XRD pattern of the activated carbon (**Figure 1(A)**) exhibited broad peaks at $2\theta = 25.02°$ and 43.52°, which are characteristic of amorphous carbon structures. These peaks can be indexed to the (002) and (100) crystal planes, respectively, indicating the presence of disordered graphitic domains within the carbon matrix. [36, 37]. The XRD pattern of Fe_3O_4-activated carbon composite (Figure 1B) exhibited peaks at $2\theta = 30.04°$, 35.40°, 43.02°, 56.94°, and 62.54°, which correspond to the (220), (311), (400), (511), and (440) crystallographic planes of Fe_3O_4, respectively. The XRD pattern confirmed the formation of magnetite Fe_3O_4 (JCPDS card No. 79-0417), similar to those reported in the literature for Fe_3O_4 particles [38,39].

These peaks confirm the successful incorporation of crystalline magnetite (Fe_3O_4) into the activated carbon matrix. However, the baseline was not flat due to the carbon background.

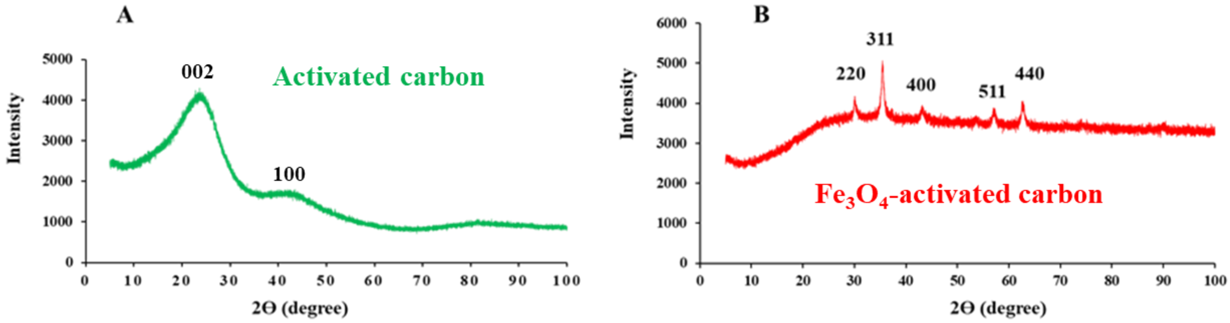

Figure 1 XRD patterns of activated carbon (A) and Fe_3O_4-activated carbon (B).

The morphology of the activated carbon and Fe_3O_4-activated carbon is depicted in **Figure 2**. The activated carbon exhibits some pores on its surface and displays a broad range of particle sizes and shapes, ranging from submicron to 125 µm. The Fe_3O_4-activated carbon shows the coverage of Fe_3O_4 over the pores and the carbon surface.

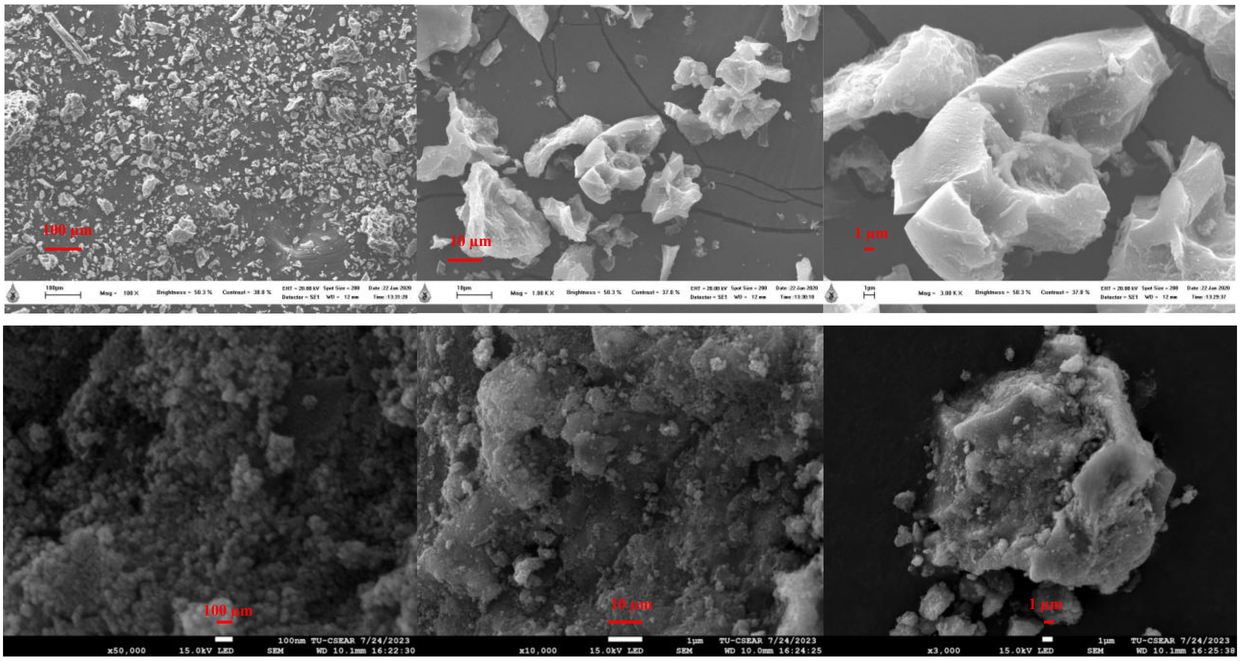

Figure 2 SEM images of activated carbon from spent coffee ground (top row) and Fe_3O_4-activated carbon (bottom row)

The contribution of Fe_3O_4 on the carbon surface is shown in **Figure 3**. **Figure 3(A)** shows the EDX mapping of iron (red dots) on the surface, and **Figure 3(B)** shows the EDX mapping of oxygen (green dots) on the surface. The distribution of iron and oxygen across the surface indicates the formation of Fe_3O_4 throughout the carbon surface, not just within the pores.

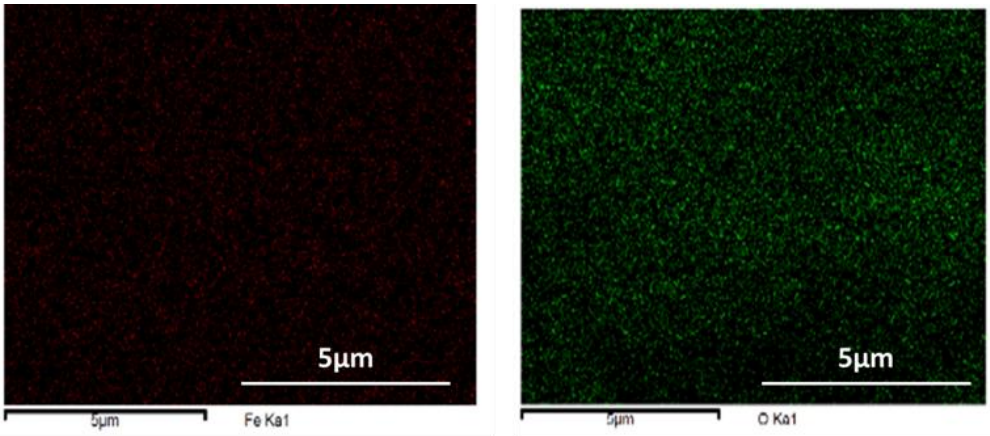

Figure 3 EDX mapping of iron (red dots) and oxygen (green dots) on the Fe_3O_4-activated carbon surface.

Figure 4 displays the surface functional groups of carbon from spent coffee grounds and Fe_3O_4-activated carbon, as identified through FTIR spectra analysis. Prior to activation, the carbon from spent coffee grounds exhibits almost no other peaks except the one at 2,360 cm^{-1}, indicating the presence of atmospheric carbon dioxide. The FTIR spectra of Fe_3O_4-activated carbon reveal broad peaks at 3,398 cm^{-1}, indicative of hydroxy groups (OH) on the surface. A peak at 1,356 cm^{-1} is also observed, further confirming the presence of hydroxy groups. The peak at 1,578 cm^{-1} corresponds to C=C stretching vibrations of alkenes, while the peaks at 630 and 590 cm^{-1} are attributed to Fe-O stretching vibrations, confirming the presence of Fe_3O_4 [40-42].

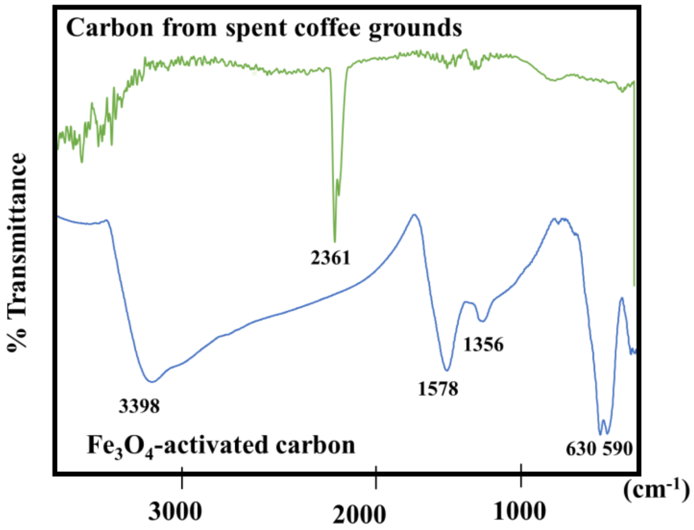

Figure 4 FTIR spectra of the carbon from spent coffee grounds and Fe_3O_4-activated carbon.

Figure 5 displays the cyclic voltammogram of the Nafion-coated SPE- Fe_3O_4-activated carbon. The voltammogram indicate a clean carbon surface without any visible impurities or peaks related to metal reduction/oxidation, suggesting the absence of metals from the carbon precursors. It is noteworthy that carbon derived from natural sources sometimes retains metals from the soil, which can persist even after pyrolysis. The absence of metal peaks in the voltammograms confirms the lack of metal impurities from the carbon source. No peaks of $Fe^{2+/3+}$ redox were observed, indicating the good stability of the magnetite on the carbon surface after 10 consecutive cyclic voltammetry scans.

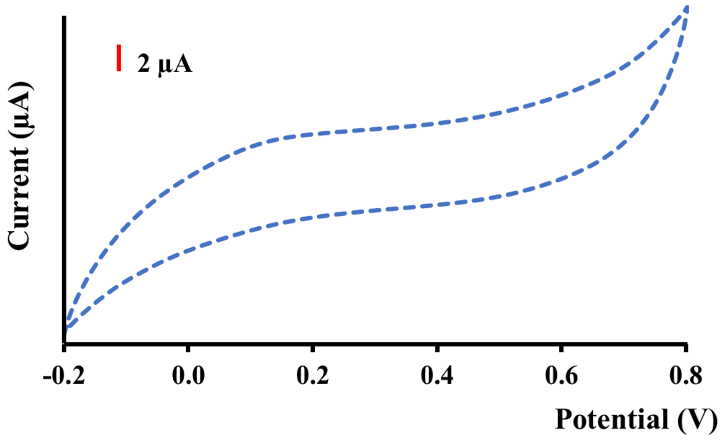

Figure 5 A cyclic voltammogram of the Nafion-coated SPE- Fe_3O_4-activated carbon. Scan rate 100 mV/s. 0.1 M phosphate buffer pH 7.4.

Typical oxygen-containing species commonly found on activated carbon surfaces include lactone, anhydride, ether, carboxyl, phenol, and carbonyl or quinone groups [26,28,43]. The FTIR results suggest the presence of hydroxy groups, which are important for surface reactivity and potential applications of the modified electrode. The presence of oxygen-containing surface functionalities on carbon, such as lactone, anhydride, ether, carboxyl, phenol, and carbonyl or quinone groups, plays a crucial role in enhancing the redox behavior of the material [26]. Moreover, the choice of electrolyte also plays a crucial role in determining the specific contribution of the oxygen-containing surface functionalities to the overall capacitance behavior and electron transfer rate of the material. In this study, the redox couple $Ru(NH_3)_6^{2+/3+}$ was utilized to investigate the influence of Nafion on the surface of Fe_3O_4-activated carbon. Activated carbons generally contain approximately 5% - 10% of oxygen-containing species, leading to a negatively charged surface. Although $Ru(NH_3)_6^{2+/3+}$ is not specifically sensitive to any particular surface functional group, its current response on surfaces with higher negative charges (more oxygen-containing species) would be higher compared to surfaces with lower oxygen-containing species. This disparity in current arises due to the electro-attractive force between $Ru(NH_3)_6^{2+/3+}$ and the negative species present on the activated carbon surface. The Randles-Sevcik equation is employed to describe the current response (I_p) of a redox reaction at an electrode [44]. It is expressed as:

$$I_p = 0.4463\, n^{3/2} F^{3/2} A D_0^{\ ½} C_0 v^{1/2} / (RT)^{1/2} \qquad (1)$$

where: I_p is the current (A); n is the number of electrons transferred; F is the Faraday constant; A is the electrode surface area (cm^2); D_0 is the diffusion coefficient of the electroactive species (cm^2/s); C_0 is the bulk concentration of the electroactive species (mol/cm^3); v is the scan rate (V/s); R is the gas constant; T is the temperature (K).

The Randles-Sevcik equation aids in analyzing the redox kinetics and understanding the factors influencing the current response during cyclic voltammetry experiments. In this particular investigation, it helps in evaluating how the Nafion coverage and the oxygen-containing species on the carbon surface impact the electrochemical behavior of the $Ru(NH_3)_6^{2+/3+}$ redox couple. By comparing the current responses of $Ru(NH_3)_6^{2+/3+}$ on the surface, valuable insights can be obtained regarding the effect of Nafion and its interaction with Fe_3O_4-activated carbon surface.

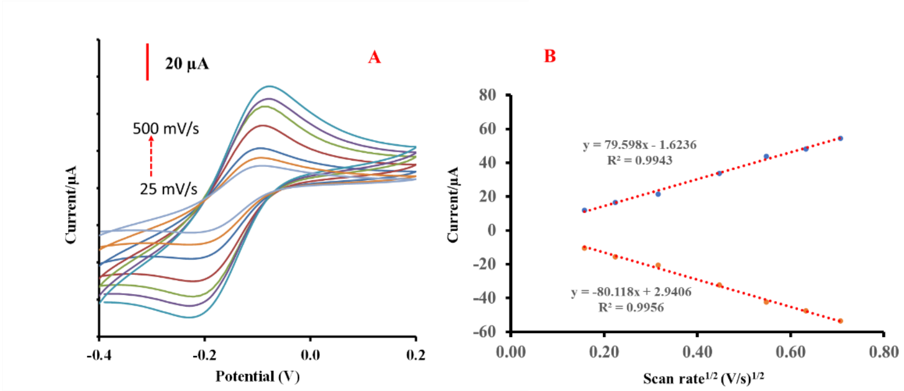

Figure 6 Cyclic voltammograms of 10 mM $Ru(NH_3)_6^{2+/3+}$ in 0.1 M KCl at various scan rates: 25, 50, 100, 200, 300, 400, and 500 mV/s (A). The plot of the peak current (I_p) versus the square root of the scan rate (B).

The magnitude of the anodic and cathodic currents at each scan rate are approximately equal, confirming a reversible redox reaction of $Ru(NH_3)_6^{2+/3+}$ on the electrode surface. Furthermore, the plot of the peak current (I_p) versus the square root of the scan rate is linear (**Figure 6(B)**), indicating a diffusion-controlled reaction of $Ru(NH_3)_6^{2+/3+}$. The linearity of the plot suggests that the Nafion coating does not hinder the accessibility of $Ru(NH_3)_6^{2+/3+}$ to the surface of the electrode within the time scale of the scan rate. The rate of electron transfer (k^0) can be calculated using Eq. (2) [45]:

$$\Psi = k^0 / [\pi D_o v[F/RT]]^{1/2} \qquad (2)$$

where Ψ is a dimensionless rate parameter. The value of Ψ with a potential difference (ΔE) of 105 mV (**Figure 6(A)**) is 0.5. The electrode area is 0.031 cm^2. For the redox couple $Ru(NH_3)_6^{2+/3+}$, the number of electrons transferred (n) is equal to 1. The diffusion coefficient (D_0) at 25 °C is 0.55×10^{-5} cm^2/s, and the scan rate (v) used in the experiment is 0.2 V/s. The bulk concentration of $Ru(NH_3)_6^{2+/3+}$ (C_0) is 10 mM. By substituting these values into Equation 2, the calculated k^0 for the redox reaction of $Ru(NH_3)_6^{2+/3+}$ on the Nafion-coated SPE-Fe_3O_4-activated carbon surface is determined to be 5.80×10^{-3} cm/s.

Comparing this calculated k^0 value to those reported for other electrode materials, the electron transfer rate on the Nafion-coated SPE-Fe_3O_4-activated carbon surface is somewhat higher than that on the highly oriented pyrolytic graphite (HOPG) edge plane. However, it is considerably lower compared to values reported for materials such as platinum, glassy carbon, and carbon fibers, which typically exhibit higher values ranging from 0.1 to 0.8 cm/s [26]. The results suggest that while coating Nafion over the Fe_3O_4-activated carbon surface does not hinder the electron transfer the electrode, it does slow down the electron transfer rate to some extent. This difference in electron transfer kinetics is likely due to the specific surface properties and functional groups introduced by the Nafion coating, influencing the electrochemical behavior of the redox reaction.

Dopamine detection on Nafion-coated SPE-Fe_3O_4-activated carbon (NMC-SPE)

Analysis of dopamine in human fluids faces interference from ascorbic acid and uric acid, which have oxidation peaks at about the same potential as dopamine on several solid electrode surfaces. Considering the pKa values of dopamine, uric acid, and ascorbic acid (8.93, 4.17 and 5.40, respectively), at pH 7.4 (close to the pKa2 of phosphoric acid), ascorbic acid and uric acid exist in their negative forms, while dopamine exists in its positive form. At this pH, Nafion behaves as a negatively charged polymer, which repels the anionic species of ascorbic acid, thereby minimizing its electrochemical response. This pH selection and Nafion coating strategy could help in the simultaneous determination of dopamine and uric acid, reducing interference from ascorbic acid in the analysis. **Figures 7(A)** and **7(B)** display cyclic voltammograms of a mixture of 50 µM ascorbic acid, dopamine, and uric acid on SPE and Nafion-coated SPE-Fe_3O_4-activated carbon, respectively. On SPE, the oxidation peak of the mixture appears at 280 mV, and the reduction peak appears at 80 mV (dashed line, **Figure 7(A)**). For Nafion-coated SPE-Fe_3O_4-activated carbon, the oxidation peaks of dopamine and uric acid appear at 280 and 320 mV, respectively. The reduction peak of dopamine appears at 80 mV without the reduction peak of uric acid. The peak at 10 mV is the reduction peak of dopamine derivatives. There is no oxidation-reduction peak of ascorbic acid.

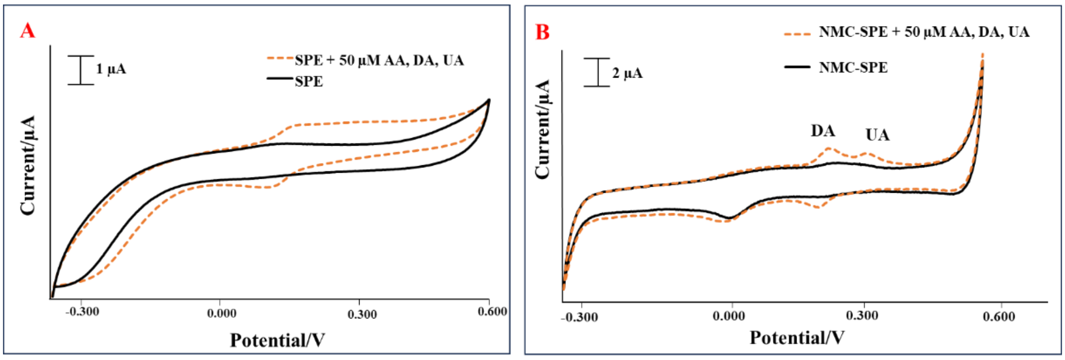

Figure 7 Cyclic voltammograms of SPE (A) and NMC-SPE (B) in 50 µM AA, DA, and UA. 0.1 M phosphate buffer pH 7.4. Scan rate 100 mV/s.

Square wave voltammograms of the Nafion-coated SPE-Fe_3O_4-activated carbon at different concentrations of uric acid (ranging from 0 to 2,000 µM) in the presence of 50 µM of dopamine and 50 µM of ascorbic acid are shown in **Figure 8(A)**. **Figure 8(B)** shows square wave voltammograms of the Nafion-coated SPE-Fe_3O_4-activated carbon at different concentrations of dopamine (ranging from 0 to 1,325 µM) in the presence of 50 µM of ascorbic acid and uric acid. The oxidation peaks of uric acid and dopamine at different concentrations were not shifted as the concentrations increased, indicating sufficient mass transport through the Nafion layer.

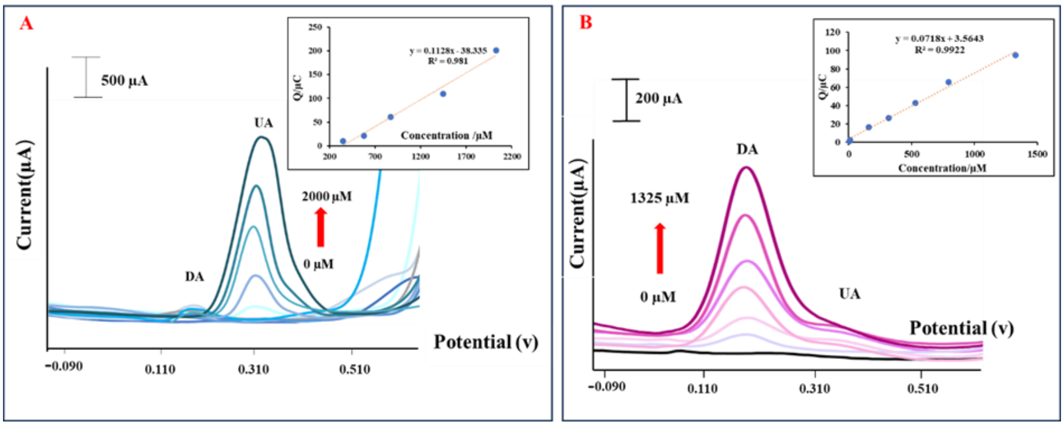

Figure 8 Square wave voltammograms of NMC-SPE in 50 µM of AA and DA and 300, 500, 750, 1,250, and 2,000 UA (A) and 50 µM AA and UA, and 1, 120, 320, 530, 800, and 1,325 µM DA. The baseline is 0.1 M phosphate buffer pH 7.4 without AA, DA, and UA. The insets show the calibration curves from the voltammograms.

Generally, when an electrode surface is covered with some polymer, the diffusion of species to and from the electrode surface can be affected. As the concentration of the species increases, the diffusion process could become more pronounced due to increased concentration gradients. This can lead to changes in the rate of mass transport of the species to the electrode surface, resulting in shifts in the peak potential observed in the square wave voltammograms. However, in this work, Nafion was mixed with Fe_3O_4-activated carbon. Some of the Fe_3O_4-activated carbon surface would be coated with Nafion, and some would not be coated. Overall, Nafion did not hinder the permeation of uric acid and dopamine to and from the electrode surface. Nafion plays a crucial role in improving the selectivity and sensitivity of electrochemical dopamine sensors, especially in the presence of common interferents like ascorbic acid and uric acid. The primary mechanism is charge discrimination or permselectivity. Nafion's structure consists of a hydrophobic fluorocarbon backbone and hydrophilic sulfonic acid groups. In an aqueous solution, these sulfonic acid groups dissociate to form anions creating a negatively charged network within the polymer. This network acts as a selective filter. Since dopamine is a positively charged cation at pH 7.4, it is electrostatically attracted to and pre-concentrated within the Nafion film, leading to an amplified signal. In contrast, common interferents like ascorbic acid and uric acid are negatively charged anions at this pH, and they are repelled by the negative charges in the Nafion film. This repulsion prevents or reduces the interferents from reaching the electrode surface, effectively suppressing their electrochemical signal. This selective accumulation of dopamine while excluding interferents significantly improves the signal-to-noise ratio and allows for the accurate detection of dopamine even at very low concentrations. The use of a Nafion film also helps to prevent electrode fouling by non-specific adsorption of larger biomolecules, enhancing the long-term stability and reproducibility of the sensor.

The electrode response for uric acid exhibits a linear relationship within the concentration range of 50 - 2,000 µM ($R^2 = 0.981$). The response for dopamine, on the other hand, ranges from 1 to 1,325 µM ($R^2 = 0.992$). The detection limit for dopamine is calculated to be 0.92 µM using Eq. (3) [46], which is comparable to those reported for other modified electrodes incorporating graphene, graphene oxide, or metal-organic frameworks, as summarized in **Table 1**.

$$Detection = \frac{3(standard\ deviation\ of\ blank\ signal)}{(slope\ of\ calibration\ curve)} \tag{3}$$

Table 1 The detection limit and linear range of different modified electrodes.

Electrode	Detection limit (µM)	Linear range (µM)	References
SPE-Fe_3O_4-carbon	0.92	1 - 1,325	This work
PEDOT-GO	2.0	6.0 - 200	[47]
Au-Cu_2O/rGO	3.9	10 - 90	[48]
N-rGO	1.5	3 - 70	[49]
Kraft paper-LIG	2.99	1 - 100	[50]
Au-HOFs	0.1	1 - 100	[12]

The successful detection of dopamine in human serum samples using Nafion coated SPE-Fe_3O_4-activated carbon demonstrates its potential for real sample analysis. The electrode's performance is evaluated based on recovery and reproducibility, as shown in **Table 2**. The specific response to dopamine is crucial in the analysis of real samples, as it ensures that the electrode is selective and capable of accurately detecting dopamine even in the presence of other interfering substances, such as ascorbic acid and uric acid. The good recovery and reproducibility of the electrode's response further support its reliability for real sample analysis. Recovery indicates how well the electrode can quantify the actual amount of dopamine in the sample, while reproducibility reflects the consistency of the electrode's response across multiple measurements.

Table 2 Dopamine detection in human serum sample.

Sample	Added (µM)	Found (µM)	Recovery (%)	RSD (%)
Human serum	30	28.82 ± 0.65	96.06	2.26
	60	60.61 ± 3.45	101.20	5.70
	120	120.74 ± 0.43	100.62	0.36

Reproducibility and stability of Nafion-coated SPE-Fe_3O_4-activated carbon

The reproducibility of the electrode preparation method was assessed by creating ten independent electrodes. Each electrode was used to perform 3 separate measurements on a sample containing 50 µM dopamine (DA), 50 µM uric acid (UA), and 50 µM ascorbic acid (AA). The results showed low relative standard deviation (RSD) values of 2.12% for DA and 3.04% for UA, indicating good reproducibility of the electrode preparation method. No response was observed for 50 µM AA during the reproducibility tests.

The long-term stability of the electrode was assessed by monitoring its response to solutions containing 50 µM DA, 50 µM UA, and 50 µM AA over a period of 14 days. After this period, the sensor retained 97.6% of its initial response for DA and 98.2% for UA, demonstrating excellent stability. Consistent with the reproducibility test, no response was detected for 50 µM AA.

The use of spent coffee grounds to produce the activated carbon electrode offers a highly cost-effective and environmentally conscious alternative to conventional, commercially available sensors. This waste-to-value approach aligns with the principles of a circular economy by valorizing a common agricultural byproduct that would otherwise contribute to landfill waste. The abundance and low cost of the raw material, combined with relatively simple and scalable preparation methods, make this modified electrode a competitive and economically viable alternative to other modified electrodes and commercial sensors, addressing both performance and environmental concerns.

Despite these advantages, there are certain limitations to consider for practical applications. Specific chemicals, such as glucose and other structurally similar neurotransmitters, have not yet been investigated, which may affect the electrode's selectivity in complex biological environments. Additionally, the use of acid activation raises concerns regarding environmental sustainability, highlighting the need for greener activation methods in future studies. Future work could focus on optimizing the morphology and porosity of the activated carbon by exploring different pyrolysis conditions or green activation methods, such as electrochemical activation or pyrolysis in the presence of carbon dioxide. These approaches may enhance pore development and increase the specific surface area, thereby providing more active sites and improving the electrode's sensitivity. Additionally, the potential of this modified electrode for the simultaneous electrochemical detection of other clinically relevant neurotransmitters or biomolecules, such as serotonin and L-dopa, could be investigated to demonstrate its versatility and applicability as a multi-analyte sensing platform.

Conclusions

In this study, Nafion coated Fe_3O_4-activated carbon electrodes were developed using carbon derived from spent coffee grounds, a sustainable approach to valorize agricultural waste. The activated carbon was characterized by X-ray diffraction and scanning electron microscopy, confirming the successful integration of Fe_3O_4 onto the carbon surface. Fourier transform infrared spectroscopy revealed the presence of oxygen-containing functional groups crucial for enhancing electrochemical responses. The modified electrodes exhibited excellent performance in detecting dopamine, demonstrating high sensitivity and selectivity against interfering substances like ascorbic acid and uric acid. This modified electrode exhibits a linear response in the concentration range of 1 to 1325 µM, with a detection limit of 0.92 µM. This detection limit is comparable to those of other modified electrodes. These findings suggest that the modified carbon electrode holds promise as a competitive and effective alternative to other modified electrodes for dopamine detection.

Acknowledgements

The financial support provided by Mae Fah Luang University (Grant No. 652A01034) is greatly appreciated. We also thank the staff of the Scientific and Technological Instruments Center at Mae Fah Luang University, Thailand for their assistance with operating the FE-SEM, XRD, and FTIR.

Declaration of generative AI in scientific writing

No content generation or data interpretation was performed by AI. The authors take full responsibility for the content and conclusions of this work.

CRediT author statement

Tharaton Nooin: Investigation; Verification; Visualization; Writing - Review & Editing. **Thaneeya Hawiset**: Investigation; Verification; Visualization; Writing - Review & Editing. **Prachak Inkaew**: Conceptualization; Verification; Writing - Original Draft; Writing - Review & Editing; Project administration; Funding acquisition.

References

[1] B Ferry, EP Gifu, I Sandu, L Denoroy and S Parrot. Analysis of microdialysate monoamines, including noradrenaline, dopamine and serotonin, using capillary ultra-high performance liquid chromatography and electrochemical detection. *Journal of Chromatography B* 2014; **951**, 52-57.

[2] J Wen, L Zhou, L Jin, X Cao and BC Ye. Overoxidized polypyrrole/multi-walled carbon nanotubes composite modified electrode for *in vivo* liquid chromatography - electrochemical detection of dopamine. *Journal of Chromatography B* 2009; **877(20-21)**, 1793-1798.

[3] T Yoshitake, J Kehr, S Yoshitake, K Fujino, H Nohta and M Yamaguchi, Determination of serotonin, noradrenaline, dopamine and their metabolites in rat brain extracts and microdialysis samples by column liquid chromatography with fluorescence detection following derivatization with benzylamine and 1,2-diphenylethylenediamine. *Journal of Chromatography B* 2004; **807**, 177.

[4] N Alizadeh and A Salimi. Polymer dots as a novel probe for fluorescence sensing of dopamine and imaging in single living cell using droplet microfluidic platform. *Analytica Chimica Acta* 2019; **1091**, 40-49.

[5] X Liu, X Hou, Z Li, J Li, X Ran and L Yang. Water-soluble amino pillar[5]arene functionalized gold nanoclusters as fluorescence probes for the sensitive determination of dopamine. *Microchemical Journal* 2019; **150**, 104084.

[6] X Wei, Z Zhang and Z Wang. A simple dopamine detection method based on fluorescence analysis and dopamine polymerization. *Microchemical Journal* 2019; **145**, 55.

[7] J JH An, DK Choi, KJ Lee and JW Choi. Surface-enhanced Raman spectroscopy detection of dopamine by DNA targeting amplification assay in Parkisons's model. *Biosensors and Bioelectronics* 2015; **67**, 739-746.

[8] S Baluchova, A Taylor, V Mortet, S Sedlakova, L Klimša, J Kopeček, O Hák and K Schwarzová-Pecková. Porous boron doped diamond for dopamine sensing: Effect of boron doping level on morphology and electrochemical performance. *Electrochimica Acta* 2019; **327**, 135025.

[9] MLB Figueiredo, CS Martin, LN Furini, RJG Rubira, A Batagin-Neto, P Alessio and CJL Constantino. Surface-enhanced Raman scattering for dopamine in Ag colloid: Adsorption mechanism and detection in the presence of interfering species. *Applied Surface Science* 2020; **522**, 146466.

[10] CX Shi, ZP Chen, Y Chen, Q Liu and RQ Yu. Quantification of dopamine in biological samples by surface-enhanced Raman spectroscopy: Comparison of different calibration models. *Chemometrics and Intelligent Laboratory Systems* 2017; **169**, 87.

[11] G Sridharan, RV Murugan, R Atchudan, S Arya and AK Sundramoorthy. Electrochemical detection of dopamine using green synthesized gold nanoparticles from strobilanthes Kunthiana's leaf extract. *Nano LIFE* 2024; **15**, 2450015.

[12] X Xu, X Liu, K Wang, Y Tang and P Miao. Electrochemical detection of dopamine based on hydrogen-bonded organic frameworks modified interface. *Langmuir* 2025; **41(21)**, 13523.

[13] S Korkmaz and AD Mülazımoğlu. Highly sensitive square wave adsorptive stripping voltammetric determination of dopamine in

human plasma using a cytosine-modified pencil graphite electrode. *ACS Omega* 2025; **10**, 23461.

[14] M Amiri, S Dadfarnia, AMH Shabani and S Sadjadi. Non-enzymatic sensing of dopamine by localized surface plasmon resonance using carbon dots-functionalized gold nanoparticles. *Journal of Pharmaceutical and Biomedical Analysis* 2019; **172**, 223.

[15] TS Anirudhan, S Alexander and A Lilly. Surface modified multiwalled carbon nanotube based molecularly imprinted polymer for the sensing of dopamine in real samples using potentiometric method. *Polymer* 2014; **55,** 4820.

[16] G Eom, C Oh, J Moon, H Kim, MK Kim, K Kim, JW Seo, T Kang and HJ Lee. Highly sensitive and selective detection of dopamine using overoxidized polypyrrole/sodium dodecyl sulfate-modified carbon nanotube electrodes. *Journal of Electroanalytical Chemistry* 2019; **848**, 113295.

[17] G Wang, T Tang, R Liu, J Li, Y Xu and S Liao. Novel electrochemical sensor based on Cu-MOF/MWCNT-COOH for the simultaneous detection of ascorbic acid and dopamine. *Langmuir* 2025; **41**, 4102.

[18] N Dükar, S Tunç, K Öztürk, S Demirci, M Dumangöz, MS Çelebi and F Kuralay. Highly sensitive and selective dopamine sensing in biological fluids with one-pot prepared graphene/poly(o-phenylenediamine) modified electrodes, *Materials Chemistry and Physics* 2019; **228**, 357.

[19] X Hui, X Xuan, J Kim and JY Park. A highly flexible and selective dopamine sensor based on Pt-Au nanoparticle-modified laser-induced graphene. *Electrochimica Acta* 2019; **328**, 135066.

[20] X Yuan, XW Wu, S Li, R Liu and Y Ling. A portable microelectrochemical sensor based on potentiostatic polarization-treated and laser-induced graphene for the simultaneous determination of ascorbic acid, dopamine, and uric acid. *Langmuir* 2024; **40**, 25529.

[21] S Lisnund, V Blay, K Chansaenpak, J Monkrathok and P Pinyou. Simultaneous electrochemical determination of dopamine, acetaminophen, and caffeine with a PVP/rGO-modified electrode. *ACS Omega* 2025; **10(28)**, 30717.

[22] K Tyszczuk-Rotko, I Jaworska and K Jędruchniewicz. Application of unmodified boron-doped diamond electrode for determination of dopamine and paracetamol. *Microchemical Journal* 2019; **146**, 664.

[23] C Li, X Chen, Z Zhang, J Tang and B Zhang. Gold nanoparticle-DNA conjugates enhanced determination of dopamine by aptamer-based microcantilever array sensor. *Sensors and Actuators B: Chemical* 2018; **275**, 25.

[24] DK Nguyen and CH Jang. Label-free liquid crystal-based biosensor for detection of dopamine using DNA aptamer as a recognition probe. *Analytical Biochemistry* 2020; **605**, 113807.

[25] H Wu, X Ding, W Li, H Liu, M Duan, Y Lei, G Wei and L Guo. Nitrogen pyrolysis-induced enhancement of active sites in an algae residue for an electrochemical dopamine biosensor. *Langmuir* 2025; **41(13)**, 8842-8852.

[26] RL McCreery. Advanced carbon electrode materials for molecular electrochemistry. *Chemical Reviews* 2008; **108(7)**, 2646-2687.

[27] Y Li, J Zhou, J Song, X Liang, Z Zhang, D Men, D Wang and XE Zhang. Chemical nature of electrochemical activation of carbon electrodes. *Biosensors and Bioelectronics* 2019; **144**, 111534.

[28] X Li, Y Jiang, P Wang, Y Mo, W Lai, Z Li, R Yu, Y Du, X Zhang an Y Chen. Effect of the oxygen functional groups of activated carbon on its electrochemical performance for supercapacitors. *New Carbon Materials* 2020; **35**, 232.

[29] J Wang. *Analytical electrochemistry*. John Wiley & Sons, New Jersey, Unite States, 2006, p. 91-92.

[30] C Song, X Liu, M Xu, D Masi, Y Wang, Y Deng, M Zhang, X Qin, K Feng, J Yan, J Leng, Z Wang, Y Xu, B Yan, S Jin, D Xu, Z Yin, D Xiao and D Ma. Photothermal conversion of CO_2 with tunable selectivity using Fe-based catalysts: From oxide to carbide. *ACS Catalysis* 2020; **10(18)**, 10364.

[31] F Pincella, K Isozaki, R Sato, T Teranishi, H Takaya and M Nakamura. Reusable magnetite nanoparticle (Fe_3O_4 NP) catalyst for selective oxidation of alcohols under microwave irradiation. *ACS Omega* 2024; **9(23)**, 24477.

[32] L Hu, A Khaniya, J Wang, G Chen, WE Kaden and X Feng. Ambient electrochemical ammonia

synthesis with high selectivity on Fe/Fe oxide catalyst. *ACS Catalysis* 2018; **8**, 9312.

[33] Z Chen, R Patel, J Berry, C Keyes, C Satterfield, C Simmons, A Neeson, X Cao and Q Wu. Development of screen-printable nafion dispersion for electrochemical sensor. *Applied Sciences* 2022; **12**, 6533.

[34] J Lu, LT Drzal, RM Worden and I Lee. Simple fabrication of a highly sensitive glucose biosensor using enzymes immobilized in exfoliated graphite nanoplatelets nafion membrane. *Chemistry of Materials* 2007; **19**, 6240.

[35] OJ Curnick, BG Pollet and PM Mendes. Nafion®-stabilised Pt/C electrocatalysts with efficient catalyst layer ionomer distribution for proton exchange membrane fuel cells. *RSC Advances* 2012; **2(22)**, 8368-8374.

[36] NK Kalagatur, K Karthick, JA Allen, OSN Ghosh, S Chandranayaka, VK Gupta, K Krishna and V Mudili. Application of activated carbon derived from seed shells of *Jatropha curcas* for decontamination of zearalenone mycotoxin. *Frontiers in Pharmacology* 2017; **8**, 760 .

[37] X Xiubo. Dielectric parameters of activated carbon derived from rosewood and corncob. *Journal of Materials Science Materials in Electronics* 2020; **31(20)**, 19927-18084.

[38] KS Loh, YH Lee, A Musa, AA Salmah and I Zamri. Use of Fe_3O_4 nanoparticles for enhancement of biosensor response to the herbicide 2,4-dichlorophenoxyacetic acid. *Sensors* 2008; **8**, 5775.

[39] TKH Ta, MT Trinh, NV Long, TTM Nguyen, TLT Nguyen, TL Thuoc, BT Phan, D Mott, S Maenosono, H Tran-Van and VH Le. Synthesis and surface functionalization of Fe_3O_4-SiO_2 core-shell nanoparticles with 3-glycidoxypropyltrimethoxysilane and 1,1-carbonyldiimidazole for bio-applications. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 2016; **504**, 376.

[40] L Nalbandian, E Patrikiadou, V Zaspalis, A Patrikidou, E Hatzidaki and CN Papandreou. Magnetic nanoparticles in medical diagnostic applications: synthesis, characterization and proteins conjugation. *Current Nanoscience* 2015; **12(4)**, 455-468.

[41] L Zhao, M Gao, W Yue, Y Jiang, Y Wang, Y Ren and F Hu. Sandwich-structured graphene-Fe_3O_4@carbon nanocomposites for high-performance lithium-ion batteries. *ACS Applied Materials & Interfaces* 2015; **7(18)**, 9709.

[42] N Luo, Z Yang, F Tang, D Wang, M Feng, X Liao and X Yang. Fe_3O_4/carbon nanodot hybrid nanoparticles for the indirect colorimetric detection of glutathione. *ACS Applied Nano Materials* 2019; **2(6)**, 3951.

[43] MJ Bleda-Martínez, JA Maciá-Agulló, D Lozano-Castelló, E Morallon, D Cazorla-Amorós and A Linares-Solano. Role of surface chemistry on electric double layer capacitance of carbon materials. *Carbon* 2005; **43(13)**, 2677-2684.

[44] CG Zoski. *Handbook of electrochemistry*. Elsevier, Amsterdam, Netherlands, 2007.

[45] S Tanimoto and A Ichimura. Discrimination of inner- and outer-sphere electrode reactions by cyclic voltammetry experiments. *Journal of Chemical Education* 2013; **90(6)**, 778-781.

[46] DC Harris. *Quantitative chemical analysis.* 7th ed. Craig Bleyer, Missouri, United States, 2007.

[47] D Li, M Liu, Y Zhan, Q Su, Y Zhang and D Zhang. Electrodeposited poly(3,4-ethylenedioxythiophene) doped with graphene oxide for the simultaneous voltammetric determination of ascorbic acid, dopamine and uric acid. *Microchimica Acta* 2020; **187(1)**, 94.

[48] TK Aparna, R Sivasubramanian and MA Dar. One-pot synthesis of Au-Cu2O/rGO nanocomposite based electrochemical sensor for selective and simultaneous detection of dopamine and uric acid. *Journal of Alloys and Compounds* 2018; **741**, 1130-1141.

[49] P Wiench, Z González, R Menéndez, B Grzyb and G Gryglewicz. Beneficial impact of oxygen on the electrochemical performance of dopamine sensors based on N-doped reduced graphene oxides. *Sensors and Actuators B: Chemical* 2018; **257**, 143-153.

[50] S Gao, X Bian, H Bi, WQ Xing, R Su, M Liang, T Li and R You. You, Kraft-based femtosecond laser-induced graphene for electrochemical dopamine sensing. *Langmuir* 2025; **41(4)**, 2744-2752.