**ABSTRACT**

Dopamine (DA) is an important neurotransmitter in the kidney, cardiovascular system, and central nervous system, which abnormality is associated with many diseases. In this work, we synthesized a functionalized multi-walled carbon nanotube/silver nanoparticle (f-MWCNT/AgNP) nanocomposites as the biosensing material to detect DA. The SEM, EDS, and TEM characterizations indicated the success of the functionalization process with MWCNT as the base material. The values of the linear range, the limit of detection (LOD), and the selectivity of the nanocomposite were all obtained from the Differential Pulse Voltammetry (DPV) measurements. The obtained LOD value was 0.2778 μM in the linear range of 0–8 μM, which is lower than the required concentration value for detecting DA in human urine (0.3–3 μM). The biosensor’s high selectivity on DA with the presence of other human-related biofluids was also reported. These results show that f-MWCNT/AgNP nanocomposites are a promising biosensor material for the detection of DA.

**GRAPHICAL ABSTRACT**

**Introduction**

Health systems such as diagnostics, preventions, and treatments are important aspects in dealing with diseases. Nowadays, the health system still tends to be reactive where patient contacts medical personnel after they already have experienced ailments with noticeable symptoms. This approach closes the opportunities for patients to actively monitor their health condition [1]. One way to deal with these problems is the development of non-invasive sensors as diagnostic tools. This method is intended to help individuals monitor their health conditions with a simple and affordable point-of-care testing system [2]. To obtain in-depth body health information, researchers developed non-invasive sensors capable of detecting analytes in biofluid (body fluids). That way, a person can understand his/her health condition [3].
overall health condition more profoundly way up to the biomolecular level [3].

Dopamine (DA), as one of the important analytes in biofluids, works as a neurotransmitter in the kidney, cardiovascular, and central nervous system. DA is produced by the nerve cells to transmit nerve impulses and has an important role in the human body, such as regulating motion, cognitive function, and control of individual behaviour. An abnormal amount of DA in the human body can be associated with schizophrenia and Parkinson’s disease [4, 5]. DA can be found in blood, urine, and sweat biofluids. The normal DA concentrations in blood and urine are 0–0.25 nM and 0.3–3 µM, respectively.

Electrochemical biosensors have been widely researched as inexpensive devices to detect various biological analytes. Moreover, they also offer a simpler, faster, and cheaper detection of diseases than conventional laboratory methods while maintaining a high accuracy and sensitivity level. Thus, they can be a promising tool for label-free DA detection.

For developing non-enzymatic electrochemical biosensors, the sensing materials can be based on carbon materials [6, 7], metal oxide-based materials [8, 9], noble metals, or other electrocatalytic materials [10–12]. Carbon-based materials have been commonly used because of their low cost, good electron transfer kinetics, and biocompatibility. At the nanoscale, carbon nanomaterials provide a large surface area, gaining high-performance electrochemical analysis in signal amplification. Its properties support high loading capacity and mass transport of reactants [13]. Carbon nanotubes (CNTs), graphenes (GRs), nanodiamonds (NDs), and fullerenes (FRs) are widely used in biosensors [14].

Carbon nanotubes (CNTs) are one of the most used nanomaterials for electrochemical sensors due to their beneficial characteristics, such as good conductivity, large edge/basal plane ratio, non-toxicity, hollow structure, small diameter, and rapid electrode kinetics [15]. CNTs can be classified into single-walled carbon nanotubes (SWCNTs), and multi-walled carbon nanotubes (MWCNTs) [16]. Compared with SWCNTs, MWCNTs production generates higher yield and lower cost per unit, as well as higher thermochemical stability, maintaining its properties when functionalized [17]. MWCNT based sensors have been developed for biological molecule detection, such as non-enzymatic H₂O₂ [18–20], ascorbic acid [21, 22], or glucose [23, 24]. To enhance the sensor performance, such as long-term stability and selectivity, composites of two or more materials have been explored for electrode modification to study its potential synergistic effects. Higher peak current could be obtained through the proper selection of composite components, compared with each material working alone [25]. For the fabrication of electrochemical biosensors, numerous studies have been performed on MWCNT surface decoration using metal or bimetal nanomaterials [26, 27], quantum dot [28], or transition metal oxide [29].

In previous DA detection studies, MWCNT has been explored by incorporating other materials such as biopolymers, metal microelectrode, and nanocomposites [30, 31]. For example, the proposed synergistic enhancement for DA detection using MoS₂/MWCNT/PPy nanocomposites showed improved electrocatalytic activity towards DA [31]. In another study, a selective DA biosensor was developed through acid-treated MWCNT on gold electrode [32]. Metal nanoparticles have some advantages in improving CNT’s properties for electrochemical sensors, such as easy to synthesize and functionalize and having an efficient catalytic role [33]. Metal nanoparticles can contribute extraordinary electrochemical catalytic activities, sensitivity enhancement, and specificity for specific analytes [34]. Silver nanoparticles (AgNPs) modified glassy carbon electrode and showed to have enhanced determination of DA [35]. The combination of AgNPs with MWCNT gave in its high conductivity, effective catalytic behavior on DA [36], and excellent biocompatibility [33]. Utilization of MWCNT/AgNPs nanocomposite on non-enzymatic DA sensing has been reported by several researchers [4, 37, 38].

Despite these existing studies, more simple procedure for dopamine detection is required while also maintaining good sensor performance. Moreover, functionalization or pre-treatment of MWCNT is required to overcome hydrophobic properties, obstructing the homogenous dispersion in aqueous solutions [39]. Our current research discusses a composite of functionalized-MWCNT with AgNPs on a glassy carbon electrode (GCE) as electrochemical biosensors for DA detection. This nanocomposite allowed the enrichment of the electroactive surface to react with the DA analyte. Scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS), and transmission electron microscopy (TEM) were used for material characterization. As for the electrochemical testing, cyclic voltammetry (CV) and differential pulse voltammetry (DPV) were chosen to investigate its sensitivity, linearity, limit of detection (LOD), limit of quantification (LOQ), and selectivity

**Experimental section**

**Chemicals**

Multi-walled carbon nanotube (MWCNT) pure powder, nitric acid (HNO₃) 65%, sulfuric acid
(H₂SO₄) 98%, silver nitrate (AgNO₃), and Nafion™ were all purchased from Sigma-Aldrich (Singapore). D(+)-glucose (C₆H₁₂O₆, 99.5%) was purchased from Fujifilm Wako Pure Chemical Corporation (Japan). Uric acid (C₅H₄N₄O₃, ≥99%), dopamine hydrochloride (98%), and urea (NH₂CONH₂, ≥98%) were purchased from Sigma-Aldrich (Japan). Formaldehyde 38%, ethanol 100%, and ammonia 25% were obtained from the local store. These chemicals were analytical grade and used without further purification. All aqueous solution was performed using distilled water (dH₂O).

Materials characterizations

Electrochemical characteristics of the sensor material were performed using CorrTest CS350 electrochemical workstation (Wuhan Corrtest Instruments Corp., Ltd., Wuhan, China). A glassy carbon electrode (GCE, 7 mm in diameter) modified by f-MWCNT/AgNP nanocomposites served as a working electrode, while a platinum wire for the counter electrode and silver/silver chloride (Ag/AgCl) for the reference electrode. The Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Spectroscopy (EDS) images were recorded using Field Emission Scanning Electron Microscopy-Energy Dispersive X-ray Spectroscopy (FESEM-EDX, QUANTA 650), conducted for morphology structure and material composition analysis. X-Ray Diffraction (XRD) was performed using X-Ray Diffractometer Bruker D8 Advance. The nanostructure of MWCNT/AgNP nanocomposites was characterized by Transmission Electron Microscopy (TEM, TECNAI G220 S-TWIN).

Synthesis of f-MWCNT/AgNP nanocomposites

The synthesis of f-MWCNT/AgNP nanocomposites was performed according to the previously reported methods [33]. The first step was to make 40 mL solution with 3:1 ratio of HNO₃ (65%) and H₂SO₄ (98%). Subsequently, 1 g of MWNT was added to the solution, then stirred using a magnetic stirrer for 4 h at 70 °C with reflux condition. The solution was diluted with 500 mL of dH₂O. The next step was to filter and wash the solution with dH₂O using filter paper. The filtration product was dried using a furnace for 16 h at 70 °C to obtain f-MWCNT.

The nanocomposite synthesis process was started by mixing 1 g of f-MWCNT with 50 mL solution of formaldehyde 38%, ethanol, and dH₂O (3:10:10 vol%). Following this treatment, 50 mL solution of silver nitrate (35 g/L) and ammonia (25%) was added to the f-MWCNT solution with a 1:2 vol% ratio. This solution had to be added slowly to keep the pH of the solution at 8–9. After the drop-by-drop addition was complete, the solution was centrifuged at 12000 rpm for 15 min. Finally, the precipitation was filtered and washed with dH₂O, followed by drying in a furnace for 16 h at 70 °C.

Surface modification of working electrode

In this research, three different working electrodes were prepared, i.e. bare carbon electrode, f-MWCNT surface-modified electrode, and f-MWCNT/AgNP nanocomposites surface-modified electrode. Before modifying the electrode surface,
cleaning of the electrode surface was conducted. The cleaning step was done by polishing it with gesture-eight motions on droplets of diamond-alumina solutions and a regular polishing cloth pad for about 1 min. The cleaned electrode was used as the bare carbon electrode measurements before performing the surface modification step with f-MWCNT and f-MWCNT/AgNP nanocomposites through the drop-casting method. We prepared f-MWCNT and f-MWCNT/AgNP nanocomposites solution (5 mg/mL) using dH_{2}O by ultrasonication for 1 h. After the homogenous solution was obtained, 10 µL of the solution was dropped on the working electrode surface and dried at room temperature for 4 h. Afterward, 5 µL of Nafion-dH_{2}O mixture (1:5 vol%) was used to coat the modified electrode surface by the second layer drop-casting method. Finally, it was left dry at room temperature for 2 h. This coating treatment will be suppressing the disintegration of the nanocomposite during electrochemical measurement. The illustration of the surface modification process is shown in Figure 1.

### Results and discussion

**Synthesis and characterization of the f-MWCNT/AgNP nanocomposites**

The synthesis was started from functionalized-MWCNT (f-MWCNT) on reflux condition for the oxidation process of MWCNT. This functionalization process was carried out by decorating MWCNT with carboxylate functional groups, which then assisted the attachment process of the silver nanoparticles (AgNPs) by obtaining a more edge site. The next step was the synthesis of f-MWCNT/AgNP nanocomposites. The basic synthesis process was to bond AgNPs with the f-MWCNT oxygen functional groups. It started from the formation of AgNPs from silver nitrate with the help of formaldehyde and ammonia, as shown in Equations (1) and (2).

\[
2\text{AgNO}_3 + 4\text{NH}_3 \rightarrow 2[\text{AgNH}_3]_2\text{NO}_3 \quad (1)
\]

\[
2[\text{AgNH}_3]_2^+ + \text{CH}_3\text{O} + \text{H}_2\text{O} \rightarrow 2\text{Ag}(s) + 4\text{NH}_3 + \text{HCOOH} + 2\text{H}^+ \quad (2)
\]

These resulted in AgNPs, which were then bonded with the oxygen functional groups via

| Table 1. f-MWCNT composition percentages analyzed using EDS. |
| Element | Mass (%) | Atomic (%) |
|---------|----------|------------|
| C       | 89.95    | 92.26      |
| O       | 10.05    | 7.74       |

| Table 2. f-MWCNT/AgNPs composition percentages analyzed using EDS. |
| Element | Mass (%) | Atomic (%) |
|---------|----------|------------|
| C       | 75.22    | 88.08      |
| O       | 11.61    | 10.21      |
| Ag      | 13.18    | 1.72       |
covalent coordination bonds and electrostatic attractions [40, 41]. The obtained f-MWCNT/AgNP nanocomposites was then characterized using SEM and EDS, as shown in Figure 2. These characterizations were used to reveal the morphology and composition of the synthesized nanocomposites as sensor materials.

Figure 2a shows that f-MWCNT spread evenly in a thread-like shape in nano sizes and Figure 2b shows the conformity of f-MWCNT/AgNP nanocomposites material morphology. The presence of AgNPs was captured in the form of white spherical particles deposited on the thread-like f-MWCNT. The SEM images also show the conformity with other carbon nanotubes SEM characterization references [33, 42–44]. The existence of oxygen functional group and AgNPs were confirmed by the EDS spectrum result presented in Figure 2c and d and the component analysis in Tables 1 and 2. The purity of f-MWCNT and f-MWCNT/AgNP nanocomposites were also confirmed from the EDS spectra that there are no other elements detected.

The typical Raman spectra of f-MWCNTs and f-MWCNT/AgNP are depicted in Figure 3a. There are four distinct peaks for both samples of f-MWCNTs and f-MWCNT/AgNP. For f-MWCNTs, peaks at ~ 1346, 1578, 2688, and 2940 corresponding to the D band, G band, 2D band, and D + G band, respectively. As for f-MWCNT/AgNP, peaks at ~ 1348, 1585, 2693, and 2945 refer to the D band, G band, 2D band, and D + G band, respectively. The introduction of AgNPs to the MWCNT causes shifting on the bands involved. The intensity ratio of the D band and G band demonstrate the crystalline sp² domains and defect structure [45, 46]. The I_D/I_G ratio resulted from the calculation of I_D/I_G f-MWCNT and f-MWCNT/AgNP are ~1.12 and ~1.48, respectively. The I_D/I_G ratio of f-MWCNT/AgNPs is remarkably greater than the I_D/I_G ratio of f-MWCNTs, demonstrating a higher degree of defect structures of MWCNTs caused by the distribution of AgNPs on the f-MWCNTs [46, 47]. The XRD pattern of the f-MWCNT/AgNP are shown in Figure 3b, the diffraction peaks are seen at 2θ values of 38.18°, 44.28°, 64.24°, and 77.19° which correspond to the crystalline planes (111), (200), (220), and (311) of Ag metal, respectively (crystallography open database (COD) No. 1100136). Also, the observed peaks at 2θ of 25.92°, 43°, and 53.42° were related to the MWCNT properties with crystal plane reflections of C (002), C (101), and C (004), respectively (COD No. 1200017). Besides, these patterns are in good agreement with the XRD patterns of the MWCNT/AgNP composite in several reports [47–49].

The TEM images of f-MWCNT/AgNP are depicted in Figure 4a and b. The distribution of AgNPs on the surface of f-MWCNT can be clearly seen from the TEM image denoted by the spherical particles distributed on the surface of MWCNTs with diameters of 2–4 nm. The particle size distribution of AgNPs calculated by ImageJ in Figure 4c demonstrated that the mean diameter of AgNPs is 2.74 nm ± 0.05 nm. The structure of f-MWCNT has a diameter of 14–32 nm. It is observed that no isolated AgNPs emerge around f-MWCNT that signify self-assembly on the functionalized-MWCNTs.

Sensing performance of f-MWCNT/AgNP nanocomposites surface-modified electrode

The first electrochemical test in this research is the comparison of CV measurement with a scan rate value of 50 mV/s from bare carbon electrode, f-MWCNT electrode, and f-MWCNT/AgNP nanocomposite electrode in 10 mM PBS (phosphate buffer saline) pH 7.4 solution. PBS solution is chosen as the main solvent because it consists of many electrolyte ions and has a pH value resembling human physiological condition. PBS is also isotonic to human body cells, so it is often used in biosensor research. Figure 5a shows the comparison between CV measurements of the bare carbon, f-MWCNT, and f-MWCNT/AgNP nanocomposite modified electrodes. The electrodes with f-MWCNT and f-
Figure 4. TEM Result of f-MWCNT/AgNP in the scale bar of (a) 50 nm and (b) 10 nm, and (c) particle size distribution of f-MWCNT/AgNP.

Figure 5. Cyclic voltammogram of (a) Bare electrode, f-MWCNT and f-MWCNT/AgNP nanocomposite in 10 mM PBS, (b) f-MWCNT/AgNP nanocomposite with 0.1 mM increment of DA concentration from 0 to 1 mM, (c) f-MWCNT/AgNP nanocomposite with variation of scan rate from 10 to 100 mV/s, and (d) Linear regression plot of scan rate parameter to current density peak value.
MWCNT/AgNP nanocomposite modification showed increased current density throughout the potential sweep. This phenomenon shows the conductive property and the capability of f-MWCNT and f-MWCNT/AgNP nanocomposite to increase the working surface of the electrode.

Furthermore, the electrode modified with f-MWCNT/AgNP nanocomposite has one anodic peak at +0.192 V and two cathodic peaks at +0.037 V and −0.296 V. These peaks show the existence of AgNPs on the sensor material, which reacts with the electrolyte solution. The anodic peak at 0.2 V showed the oxidation of Ag⁰ to Ag⁺, while the cathodic peak at −0.1 V showed the reduction of Ag⁺ to Ag⁰ and the cathodic peak at −0.4 V showed the reduction of Ag²⁺ to Ag⁺ [50].

Anodic peak at 0.2 V: \( Ag^0 \rightarrow Ag^+ + e^- \) (3)
Cathodic peak at −0.1 V: \( Ag^+ + e^- \rightarrow Ag^0 \) (4)
Cathodic peak at −0.4 V: \( Ag^{2+} + e^- \rightarrow Ag^+ \) (5)

The CV of f-MWCNT/AgNPs nanocomposite also shows the rapid change of current density on anodic and cathodic peaks, indicating good electrochemical response and fast direct electron transfer by AgNPs onto the sensor material [50]. This result infers that AgNPs have high conductivity which can increase the direct electron transfer and electrochemical properties of f-MWCNT/AgNPs nanocomposite as an electrochemical sensor.

Response of f-MWCNT/AgNP nanocomposite to the DA analyte can be seen from CV measurements that show the linear relation between the current density value of anodic and cathodic peaks with the concentration value of DA analyte. The CV measurement used a scan rate value of 50 mV/s for the concentration of DA analyte 0.1–1 mM with the increment 0.1 mM dissolved in 10 mM PBS pH 7.4. It was stated before that the addition of AgNPs was chosen because of its high conductivity and good electrocatalytic properties with DA analyte. These properties can increase the electrochemical signal produced by the DA analyte, shown in reaction Equation (6).

\[
Ag^+ + \text{Dopamine} \left( C_8H_{11}NO_2 \right) \rightarrow Ag^+ \text{quinone} \left( C_8H_9NO_2 \right) + 2H^+ + 2e^-
\] (6)

The reduction-oxidation (redox) reaction between dopamine with Ag⁺ involved 2 protons and 2 electrons. Dopamine tends to have an oxidation reaction only to form a dopamine-o-quinone (DOQ), therefore AgNPs are needed to catalyze the redox reaction. This redox reaction produces one anodic peak and one cathodic peak (Figure 5b); both current density peak values increased linearly along with the increment of DA analyte concentration in PBS solution. Based on this redox reaction, the number of electrons released/captured will increase along with the increment of DA concentration value in the working solution. The number of electrons released/captured will affect the current density value at the anodic/cathodic peak. Furthermore, Equation (6) shows that the tendency of DA analyte to carry out oxidation reaction causes the reduction of current density value of Ag⁺ cathodic peak [35, 43].

Figure 5b also shows that the increment of current density from 2 to 3 mM was not as high as the...
increment of current density from 0 to 1 mM. This non-linearity indicates the limited number of AgNPs on the sensor material which can catalyze the redox reaction of the DA analyte. There was also a shift in anodic peak to positive potential direction from $+0.355 \text{ V (1 mM)}$ to $+0.454 \text{ V (3 mM)}$. This shift indicated the increase of energy needed to oxidize the higher number of DA analyte in the working solution [51]. Besides, the peak current ratio of the anodic and cathodic peaks was not unity, which indicated the irreversible redox reaction in this experiment. The phenomena were caused by the electrode fouling due to the deposition of oxidation products on the electrode surface [38].

To further evaluate the redox reaction mechanism and the limitation of the electron transfer process on the f-MWCNT/AgNP nanocomposites surface-modified electrode towards DA, scan rate variation measurements were conducted. Scan rate measurements on the electrode with f-MWCNT/AgNP nanocomposites were done by varying the scan rate, as shown in Figure 5c. The scan rate values used in these experiments are 10, 25, 50, 75, 100 mV/s using 1 mM DA with 10 mM PBS pH 7.4 as solvent. This scan rate variation measurement was intended to show the relation between f-MWCNT/AgNP nanocomposites current response with changing the scan rate. The linear response between these two values will show the diffusion-controlled mechanism on the sensor material surface for the electrochemical system [52].

Linear coefficient correlation ($R^2$) values from anodic peaks are 0.998 (Figure 5d), respectively. These values show a linear response of current density anodic and cathodic peaks to scan rate parameter. These results indicate the diffusion-controlled mechanism in redox reaction of DA analyte by f-MWCNT/AgNP nanocomposites [52]. The diffusion-controlled mechanism in redox reaction of DA analyte happened because the increment of the diffusion process on electrode material matches the increment of scan rate value. Figure 5c also shows that the increment of scan rate value made the redox potential peaks shift further and the current density peaks increase. Thus, these measurements show the rapid redox process and the limitation of the electron transfer process on the nanocomposite modified electrode surface.

### Table 4. Anodic peak on repeated measurement.

| Measurement Number | Anodic Peak Potential (V) | Anodic Peak Density Current (mA/cm²) | Relative Error (%) |
|--------------------|---------------------------|-------------------------------------|--------------------|
| 1                  | 0.532                     | 1.829                               | 0                  |
| 2                  | 0.522                     | 1.822                               | 0.42               |
| 3                  | 0.507                     | 1.785                               | 2.43               |
| 4                  | 0.520                     | 1.882                               | 2.86               |
| 5                  | 0.506                     | 1.807                               | 1.24               |
| 6                  | 0.524                     | 1.795                               | 1.85               |
| 7                  | 0.501                     | 1.790                               | 2.15               |
| 8                  | 0.535                     | 1.878                               | 2.68               |
| 9                  | 0.541                     | 1.937                               | 5.89               |
| 10                 | 0.546                     | 1.984                               | 8.48               |
| Average Relative Error |                           |                                     | 2.80               |

**Figure 7.** Combined differential pulse voltammogram signal of 10 mM glucose, 500 mM urea, 10 mM uric acid, 1 mM DA in 10 mM PBS.

The sensitivity of f-MWCNT/AgNP nanocomposites to dopamine

DPV method was used to calculate the sensitivity parameters, i.e. the limit of detection (LOD) and the limit of quantification (LOQ). The scan rate of 50 mV/s, increment of 1 mV, amplitude of 10 mV, pulse width of 0.05 s, and pulse period of 0.2 s are the parameters that we used for DPV method. The sensitivity was studied in DA solution made in buffer (PBS pH 7.4) with concentration 1; 2; 3; 4; 6; 8; 10; 12; 14 μM (Figure 6a). Electrochemical sensor sensitivity is one of the static characteristics that compares the changes of measured concentration value with the changes of concentration value. The changes of measured concentration value can be calculated from the increment of current density from the DPV measurement. This relationship indicates that the sensitivity of the electrochemical sensor material can be obtained from the gradient of the
linear regression equation, where C is the concentration of the DA.

\[ I = 0.0058 \times C - 4.394 \times 10^{-4} \] (7)

The equation shows that the sensitivity value of the f-MWCNT/AgNP nanocomposites electrochemical system is 0.0058 mA cm\(^{-2}\) \(\mu\)M\(^{-1}\) on the anodic peak. The linearity of the electrochemical system shows a linear relationship between the measured value to the input value. This linear relationship usually appears in certain linear ranges. Figure 6b shows that the linear range for the anodic peak is from 1 to 8 \(\mu\)M with a coefficient correlation value (R\(^2\)) of 0.998. These high coefficient correlation values show good linearity from the f-MWCNT/AgNP nanocomposites sensor material at the anodic [51–53].

Limit of detection (LOD) is the value of minimum analyte concentration, which can give an analyte-detected signal significantly different from background or noise signal. From the linear regression equation and signal-to-noise ratio of 3, the LOD value can be obtained as following [54],

\[ LOD = \frac{3S_b}{m} \] (8)

Standard deviation \(S_b\) can be obtained by conducting 5 DPV measurements in a blank solution (10 mM PBS pH 7.4). As for the value of \(m\), it can be obtained from the gradient of the linear regression equation (sensitivity value). From this equation, the LOD value at anodic peaks is 0.2778 \(\mu\)M. It was stated that the normal DA concentration in urine is 0.3–3 \(\mu\)M. LOD values from DPV measurement are lower than the minimum DA concentration value in urine [2, 55, 56].

Table 3 shows the comparisons between linear range and LOD values in this research with the other similar works. From this, the linear range from this research is narrow compared to other works. Nevertheless, it can also be seen that the LOD value in this research performance is well compared to other LOD values.

**Reproducibility and selectivity**

The reproducibility was determined through repeated measurements. The repeated measurement of sensor material was conducted in 1 mM DA mixed with the 10 mM PBS pH 7.4 as the solvent. This measurement is intended to check f-MWCNT/AgNP nanocomposites stability by calculating the differences between current density peak values of repeated measurement. These differences are calculated in relative error percentages. Relative error percentages are obtained with Equation (9). The relative error percentages from 10 repeated measurements using CV method are obtained from this equation. The relative average error percentage on the anodic peak was 2.80% (Table 4).

\[
|Relative Error| = \frac{|current\ density - reference\ current\ density|}{reference\ current\ density} \times 100\% 
\] (9)

Sensor selectivity measurement with DPV method is intended to show the capability of the f-MWCNT/AgNP nanocomposites in recognizing DA with other analyte interferences. This measurement is done by adding 10 mM of glucose, 500 mM of urea, and 10 mM of uric acid to 1 mM DA in 10 mM PBS pH 7.4 solution. These interference concentrations are chosen based on their concentration in human urine. Figure 7 shows the selectivity properties of f-MWCNT/AgNP nanocomposites to DA with glucose, urea, and uric acid analyte interferences from DPV method measurement. Glucose and urea did not show any responses, while a peak response for uric acid analyte (\(E_{pa} = 0.601\) V; \(I_{pa} = 0.0175\) mA/cm\(^2\)) appeared aside from the peak for DA analyte (\(E_{pa} = 0.421\) V; \(I_{pa} = 0.1099\) mA/cm\(^2\)). Because it has a good peak separation, DA measurement will not be affected. Thus, these results showed that the sensor material f-MWCNT/AgNP nanocomposites could selectively detect DA analyte with high current density value although with the interferences of glucose, urea, and uric acid analytes.

**Conclusions**

The synthesized electrochemical biosensors f-MWCNT/AgNP nanocomposites exhibited high sensitivity for the detection of dopamine. The CV results show that f-MWCNT/AgNP nanocomposites was capable of increasing the electrochemical response of the working electrode, which means that it showed good electrocatalytic behavior in terms of increasing electrochemical signal from DA analyte. The average relative error obtained was only 2.80% for 10 times repeated measurements. This result implied that the f-MWCNT/AgNP nanocomposites could be used to detect DA multiple times repeatedly with high sensitivity. The DPV results showed that f-MWCNT/AgNP nanocomposites had a 0.0058 mA cm\(^{-2}\) \(\mu\)M\(^{-1}\) sensitivity value, 1–8 \(\mu\)M linear range with a coefficient correlation (R\(^2\)) value of 0.998, 0.2778 \(\mu\)M LOD
value, and good selectivity to DA analyte compared to glucose, urea, and uric acid. Our synthesized f-MWCNT/AgNP nanocomposites exhibited a lower LOD value than the minimum normal DA concentration in human urine (0.3 μM). Thus, the developed nanocomposite could be promisingly used to detect real human DA analyte.

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Disclosure statement

There are no conflicts to declare.

Author contributions

IA and MH conceptualized and designed the work; LNR, RRA, and SSS performed the synthesis and characterized the materials; IA, MH, LNR, and RRA wrote the paper; SH and GG analyzed and interpreted the data; MH and BY Supervised the work.

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