Simultaneous Analysis of Dopamine and Ascorbic Acid Using Polymelamine/Gold Nanoparticle-Modified Carbon Paste Electrode

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Abstract: *Modification of electrode using polymelamine (PM) and gold nanoparticles (AuNPs) has been successfully developed via electropolymerization and electrodeposition onto carbon paste electrode (CPE) using cyclic voltammetry (CV) technique. The modified electrode (AuNPs/PM/CPE) was applied as voltammetry sensors in a simultaneous of dopamine (DA) and ascorbic acid (AA). AuNPs/PM/CPE presented an effective surface area 5 times wider than CPE and demonstrated good electrocatalytic performance in the oxidation of DA and AA in 0.1 M phosphate buffer solution (pH 3) with a scan rate of 100 mV s^{-1}. The differential pulse voltammetry (DPV) technique was chosen as the best method for separating potential peaks of DA and AA. The linear response for determining DA and AA using the DPV technique produced a concentration range of 0.1–13 and 0.4–12 μM with coefficient linearity of 0.9999 and 0.9997, the limit of detection of 0.1405 and 0.2187 μM, the accuracy of 89.62–109.16% and 83.63–105.08%, and the precision of 0.017–0.701% and 0.066–0.626%, respectively. In addition, this electrode was applied in a real sample of infant urine with a concentration of 1 μM by spike method and found 98.86 and 98.28% as percent recovery of DA and AA, respectively.*

Keywords: *ascorbic acid; dopamine; gold nanoparticles; polymelamine; voltammetry*

■ INTRODUCTION

Dopamine (DA) and ascorbic acid (AA) are natural compounds that play an important role in the metabolism of the human body [1-3]. DA is the main catecholamine that acts as a neurotransmitter in mammalian brain tissue and biological fluids and plays a very important role in the central nervous system. Abnormal concentrations of DA can be associated with indications of several disorders, such as Parkinson's disease, schizophrenia, tumors, and HIV infection [4-7]. AA is known to play a role in the metabolism and formation of DA via hydroxylation reaction [8]. Here AA acts as a cofactor [9-10]. Clinical studies showed that the AA content in the biological matrix could be used to assess excessive oxidative stress associated with cancer, diabetes mellitus, and liver disease [11-13]. Excess AA was excreted in urine, as well as DA, therefore, DA could be found in urine simultaneously with the presence of AA [14]. In the biological matrix, some studies mentioned that DA concentration in central nervous system extracellular fluid was 0.01–1.00 µM, whereas AA concentration was 100–500 µM [15]. Hence, simultaneous determination of DA and AA is important for diagnosis and observing diseases. Sensitivity and selectivity are important parameters in the development of simultaneous detection of DA and AA mixture [16-19].

Various analytical methods used for DA and AA analysis have been developed, including high-performance liquid chromatography (HPLC) [20-21], liquid chromatography-mass spectrometry tandem (LC/MS/MS) [22], spectrometry method using a microfluidic system [23], and HPLC-MS method [24]. All of these methods require temperature control, separation, spectrophotometric detection systems, equipments, and expensive operational costs. Recently, the development of voltammetry sensors has been widely undertaken for simultaneous determination of DA and AA [16,25-26] However, the electrodes used were unmodified and suffered from very high potential, which resulted in low selectivity and poor sensitivity and repeatability [24,27]. This low performance was considered to occur due to homogeneous electrocatalytic oxidation [28], very close potentials [29], overlapping potentials of DA and AA oxidation peaks [16,30], and electrode fouling [31-32].

On the other hand, oxidized DA would catalyze AA oxidation, which resulted in a single and broad peak for both analytes [33]. This phenomenon needs to be eliminated for correct DA determination. Thus, selective determination of peak DA and AA becomes the main goal of electroanalytic research. Polymers and metal nanoparticles have been used for electrode modification because polymer can be an ideal host matrix for gold nanoparticles (AuNPs) exploiting an elastic electronic charge flow through the polymer matrix in the electrochemical process [4,11]. Modification of the electrode with polymelamine (PM) by electropolymerization provided an advantage in preventing the aggregation of metal nanoparticles [34-35]. The presence of amines in carbon materials could prevent aggregation and provide high biocompatibility [36]. The electropolymerization of PM has been reported for the detection of DA [16,37].

Meanwhile, the presence of AuNPs in PM could amplify the resulting signal [36,38-39]. The presence of PM and AuNPs coated on the surface of carbon paste (CPE) has been used for the analysis of AA, UA, and DA [36,40] with good and selective results. The development of this electrode was further carried out for the analysis of mixtures of DA and AA, which are usually present together in biological fluids in relatively high concentrations. Consequently, selectivity and sensitivity are important in the manufacture of voltammetric sensors.

In this paper, we investigated the performance of AuNPs/PM/CPE as a voltammetry sensor for simultaneous detection of DA and AA. We expect to obtain a voltammetry sensor for the analysis of a mixture of DA and AA with high selectivity, sensitivity, accuracy, and low detection limits. To confirm the accuracy of the modified electrochemical sensor, a certain number of analytes was spiked into biological samples.

■ EXPERIMENTAL SECTION

Materials

Nanoporous carbon was obtained from the Research and Development Center for Forest Products Bogor, Indonesia. DA, AA, paraffin, sodium dihydrogen phosphate (NaH_2PO_4), sodium hydrogen phosphate (Na_2HPO_4), sodium acetate (CH_3COONa), sodium hydroxide (NaOH), sodium sulfate (Na_2SO_4), sulfuric acid (H_2SO_4), and acetic acid (CH_3COOH) were purchased from Merck. Pure gold and melamine were purchased from Sigma-Aldrich. Ultra-high pure water (UHP) was used throughout the experiments.

Instrumentation

All the electrochemical experiments were performed on EDAQ e-corder 410 (Australia) which was equipped with three electrodes: AuNPs/PM/CPE working electrode, Ag/AgCl reference electrode, and platinum wire as auxiliary electrode. Scanning electron micrographs (SEM-EDX) measurements were conducted to observe the surface morphology of the CPE, PM/CPE, and AuNPs/PM/CPE electrodes using FESEM Thermo Scientific Quattro S (US) and JOEL IT700 JR (US)

The electrochemical analysis was performed using different modified electrodes (AuNPs/PM/CPE, PM/CPE, AuNPs/CPE, and bare CPE) in a 0.1 M phosphate buffer solution (PBS) as a supporting electrolyte by cyclic voltammetry (CV). Conditions for DA: 10 mL of 20 µM DA solution in PBS (pH 6) with a scan rate of 100 mV s^{-1} in the potential range of –0.6 to +1.0 V. Conditions for AA: 10 mL of 20 µM DA solution in PBS (pH 7) with a scan rate of 100 mV s^{-1} in the potential range of –0.3 to +0.6 V. Conditions for simultaneous of DA and AA: 10 mL PBS (pH 3) solution containing 20 µM DA and 20 µM AA with a scan rate of 100 mV s^{-1} in the potential range of –0.3 to +0.7 V.

Procedure

Fabrication of AuNPs/PM/CPE

Electropolymerization of melamine and electrodeposition of AuNPs was performed based on previous studies [41-43] and illustrated in Scheme 1. Carbon powder and paraffin were mixed to make CPE in a ratio of 7:3, respectively. Before modification, the surface of CPE should be activated using 0.5 M H_2SO_4 by CV under a potential ranging from 0 to 1.0 V at 100 mV s^{-1} for 30 cycles. Then, electropolymerization of melamine on the surface of CPE (PM/CPE) was conducted using 0.1 M NaOH solution containing 1 mM melamine under a potential ranging from –0.1 to 1.6 V at 100 mV s^{-1} for 20 cycles. Furthermore, the deposition of AuNPs onto PM/CPE surface was realized by CV using 0.01 M Na_2SO_4 and 0.01 M H_2SO_4 solution containing 1 mM $HAuCl_4$ with a potential ranging from –0.4 to +1.5 V at a scan rate of 50 mV s^{-1} for 12 cycles, followed by rinsing thoroughly with water and maintaining the system under dry conditions.

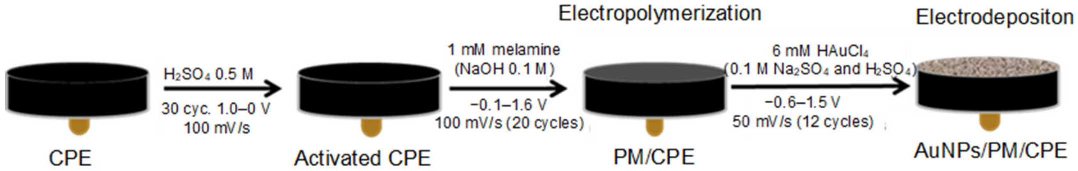
Simultaneous determination of DA and AA in real sample

To evaluate the validity and applicability of the modified electrode AuNPs/PM/CPE in the real sample, this electrode was tested in a human urine sample using the spike method. The infant urine samples were diluted 50 times using 0.1 M PBS (pH 4.0) and centrifuged at 7000 rpm for 5 min at room temperature. Certain amounts of DA and AA were added to the diluted sample and were then measured.

■ RESULTS AND DISCUSSION

Morphological Characterization of AuNPs/PM/CPE

The morphology of CPE, PM/CPE, AuNPs/CPE, and AuNPs/PM/CPE are shown in SEM images of Fig. 1 and the surface chemical composition of these electrodes are summarized in Table 1. As seen from Fig. 1(a), the surface of unmodified CPE was smooth and the EDX data displayed carbon as the dominant element. The SEM image of PM/CPE (Fig. 1(b)) showed that the aggregated structure of PM was immobilized onto the surface of CPE. The EDX data of this electrode also confirmed the presence of nitrogen elements on the surface of PM/CPE. As compared to AuNPs/PM/CPE, the presence of AuNPs through the electrodeposition process can be seen in Fig. 1(c), and the magnification of AuNPs onto PM/CPE is shown in Fig. 1(d). These results showed that the presence of PM facilitates the AuNPs to be decorated onto PM/CPE to form grassland with a spherical shape with an average size of 46.78 nm [36-44].



Scheme 1. Schematic illustration of the fabrication process of AuNPs/PM/CPE

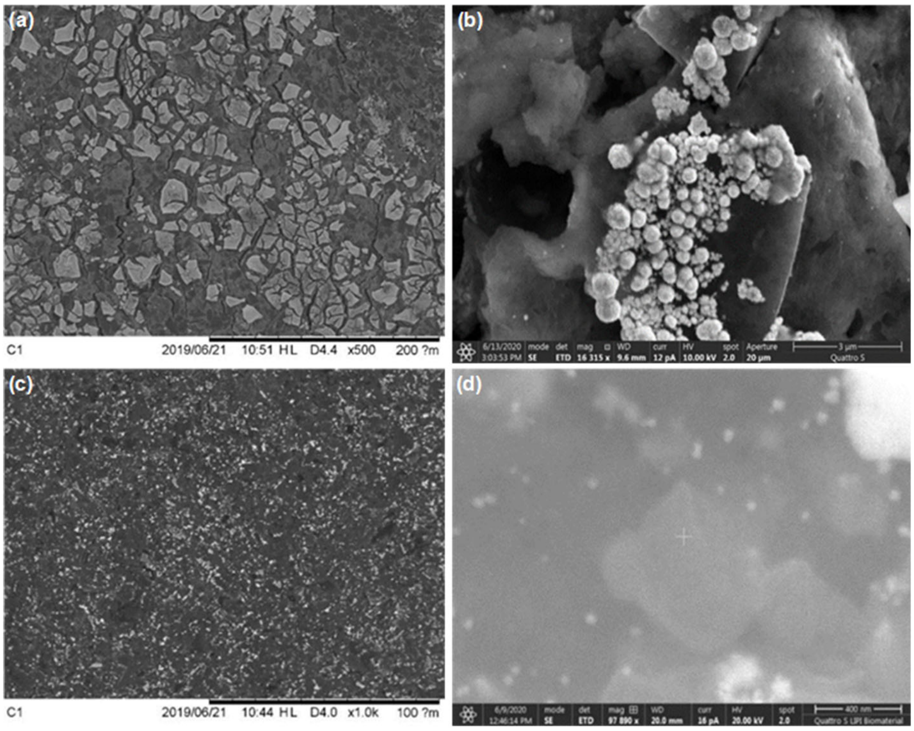


Fig 1. SEM images of (a) CPE, (b) PM/CPE, (c) AuNPs/PM/CPE, and (d) magnification of AuNPs

Table 1. The chemical composition of CPE, PM/CPE, and AuNPs/PM/CPE surface

Element number	Element symbol	Element name	CPE		PM/CPE		AuNPs/PM/CPE	
			Atomic conc.	Weight conc.	Atomic conc.	Weight conc.	Atomic conc.	Weight conc.
6	C	Carbon	93.16	91.00	62.82	53.11	69.69	22.44
8	O	Oxygen	6.74	8.77	23.50	26.47	13.03	5.59
7	N	Nitrogen	-	-	10.97	10.81	1.89	0.71
13	Al	Aluminium	-	-	-	-	0.84	0.61
14	Si	Silicon	0.10	0.23	1.55	3.06	0.78	0.59
16	S	Sulfur	-	-	-	-	0.60	0.52
35	Br	Bromine	-	-	1.16	6.55	-	-
79	Au	Gold	-		-	-	13.17	69.54

These results clearly revealed that the nanoparticles were uniformly distributed with no aggregation observed [45]. The EDX data of AuNPS/PM/CPE exhibited a decrease in nitrogen concentration and showed the presence of gold, which indicated that some of the AuNPs covered the PM surface.

The Effect of pH and Scan Rate on the Electrochemical Oxidation of DA, AA, and the Mixture of DA and AA

The effect of pH of the supporting electrolyte on the electrochemical response of DA and AA using AuNPs/PM/CPE at pH values ranging from 3 to 8 was studied and presented in Fig. 2 and 3, respectively. Fig. 2 demonstrated the effect of pH on the electrooxidation of DA in a solution containing 20 µM of DA with a scan rate of 100 mV s^{-1}. The anodic peak current (I_{pa}) of DA increased from pH 3 to 6 and slowly decreased at a pH higher than 6 (Fig. 2(a)). These observations could be correlated to the pK_a value of DA (6.8) [46-47]. In the pH range of 3 to 5, DA exists in a neutral molecular form, making it more difficult to oxidize and creating

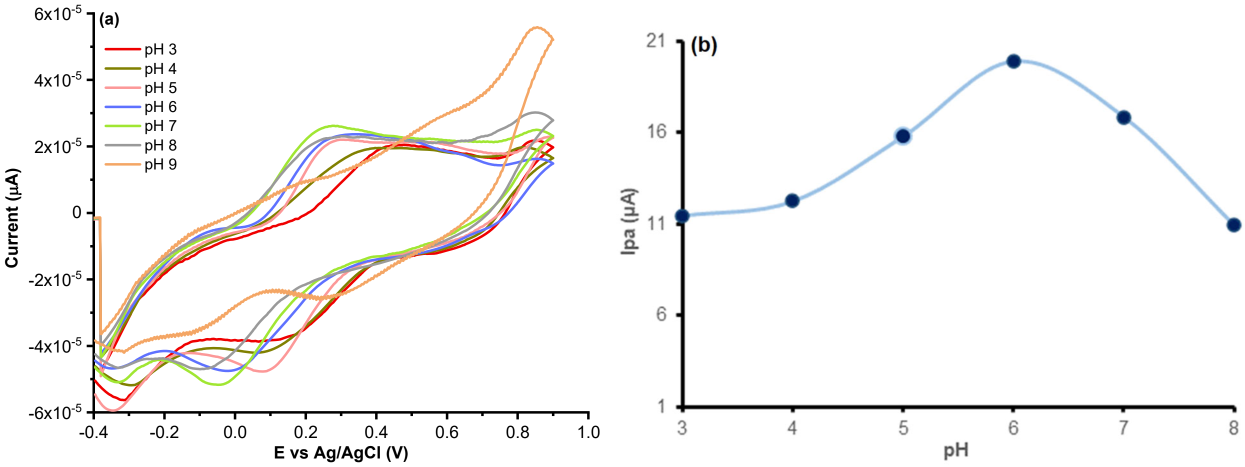


Fig 2. (a) Cyclic voltammogram of DA 20 µM with the scan rate of 100 mV s^{-1} at various pH values, and (b) plot of I_{pa} DA vs pH solution from 3 to 8

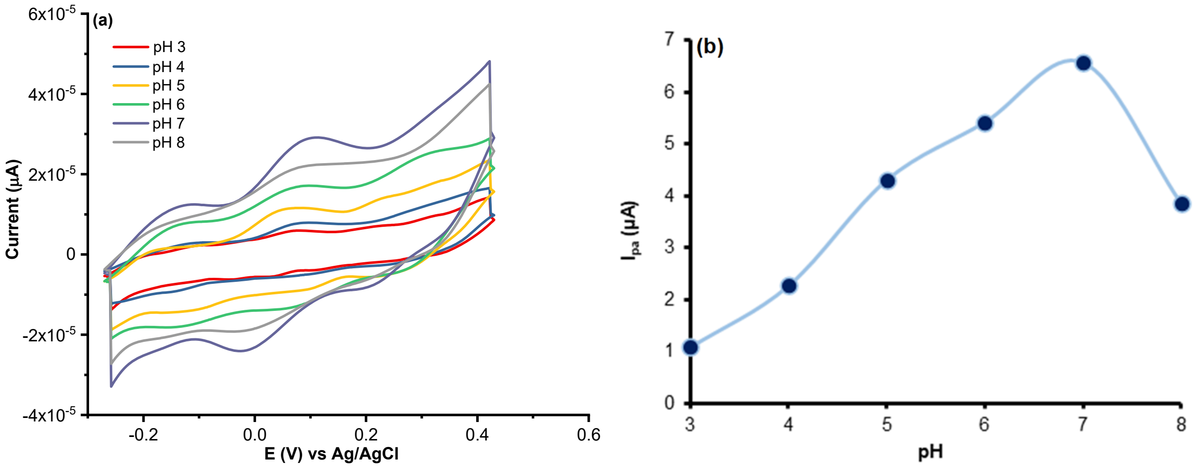
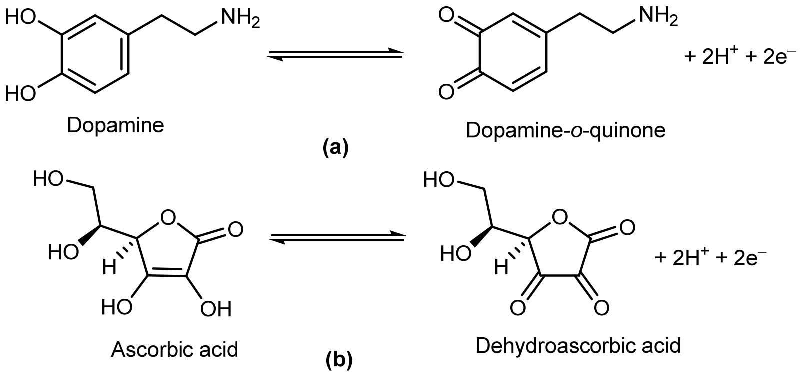


Fig 3. (a) Cyclic voltammogram of AA 20 µM with the scan rate 100 mV s^{-1} at various pH values, and (b) plot of I_{pa} AA vs pH solution from 3 to 8

less current [1,48-49]. When the pH value increased close to 6, near the pKa value of DA, DA was more easily oxidized to form DA-*o*-quinone (Scheme 2(a)). Hence, the peak current became higher. At the pH above 6, the amount of protonated DA gradually decreased until the pH reached 9 [16,50]. Hence, the optimum pH value for determining DA was pH 6.

Fig. 3(a) shows the voltammogram of AA (20 µM) measured in various pH values ranging from 3 to 8 with the scan rate of 100 mV s^{-1}. The plot of I_{pa} AA vs pH solution shown in Fig. 3(b) indicated that I_{pa} of AA was improved with the increase of pH to 7. However, the I_{pa} then decreased at pH 8. This observation might be associated with the pK_{a1} and pK_{a2} values of AA, e.g. 4.04 and 11.34, respectively [51]. At pH ≤ 4, AA was mostly protonated and, with increased pH value could increase the peak current so that it was easy to oxidize to form dehydroascorbic acid (Scheme 2(b)). However, at pH 8 there was a decrease in I_{pa} because AA turned into its salt, making it more difficult to oxidize [52-53]. Thus, pH 7 was taken as an optimum pH for determining AA. Based on Fig. 2(a) and 3(a), the anodic potential peak (E_{pa}) is shifted to the left as the pH increases in both DA and AA. This indicates that the proton is taking part in the reaction on the surface of the electrode [54-55].

The differential pulse voltammetry (DPV) technique was used to evaluate the optimum pH for the determination of simultaneous DA and AA, because it



Scheme 2. Oxidation-reduction reaction of (a) DA and (b) AA

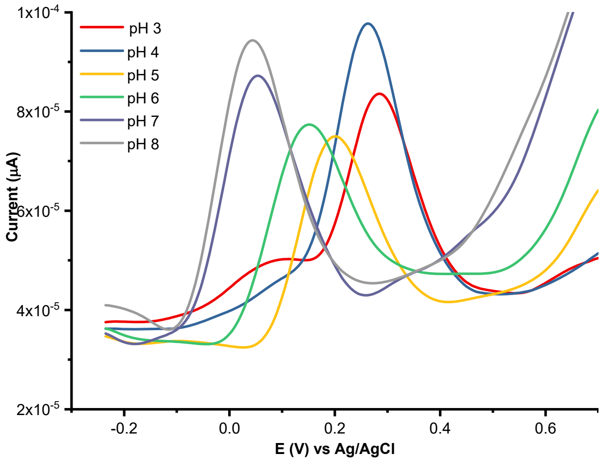


Fig 4. DPVs of DA (20 µM) in the presence of AA (20 µM) with various pH values at the scan rate of 100 mV s^{-1}

presented higher sensitivity and peak resolution. Fig. 4 shows the effect of pH on determining DA and AA. The DPVs portrayed the peak current of DA and AA at various pH values, which were mostly overlapping. Interestingly, at pH 3 the peak current of DA and AA were well-separated, indicating the potential of DA and AA of 0.282 and 0.098 V, respectively. This analysis clarified that the peak currents of DA and AA were dependent on the pH value. To obtain the measurement with high sensitivity and selectivity, pH 3 was used as the optimum pH value for simultaneous voltammetric analysis of DA and AA.

The effect of scan rate on the electrochemical oxidation of DA, AA, and the mixture of both substances was examined using CV with various scan rate values. As displayed in Fig. 5(a) and (c), the oxidation peak currents of DA and AA were increased linearly with the increase in scan rate. Moreover, the reactions that occur on the surface of the electrode can be known from the slope value of the plot between log I_p and log v (Fig. 5(b) and (d)). The regression equation of DA and AA was found I_{pa} = 0.8624 log v – 0.6037 (R^2 = 0.9605) and I_{pa} = 0.6814 log v – 0.3385 (R^2 = 0.9787), respectively. The results show that the values of redox peak currents (I_{pa} and log v) were improved linearly with the increase of scan rate close to 1, 0.9605 (DA) and 0.9787 (AA). These results indicated that the electrochemical oxidation of DA and AA at AuNPs/PM/CPE was a diffusion control reaction [56]. For, the slope values of DA and AA were between 0.5 and 1.0. This indicates that the reaction that occurs on the surface of the electrode is a mixed reaction of diffusion and adsorption, but the dominant process is diffusion [57-58].

In Fig. 5(e), CV response of simultaneous DA and AA indicated that when the scan rate was higher, the anodic peak current (I_{pa}) of DA was also higher. On the other hand, I_{pa} of AA was lower. At the scan rate of 100 mV s^{-1} (Fig 5(f)), the potential peaks of DA and AA were well-separated as compared to the other scan rates. This observation occurred because at the scan rate of 100 mV s^{-1} the value of I_{pa} obtained reached its highest (6.04 A). Therefore, the optimum scan rate for the simultaneous analysis of DA and AA mixture was selected to be 100 mV s^{-1}.

Electrochemical Behavior of Individual Determination of AA, DA, and Their Mixture

The electrocatalytic activity of bare CPE, PM/CPE, AuNPs/CPE, and modified electrode AuNPs/PM/CPE toward the oxidation of DA, AA, and the mixture of DA

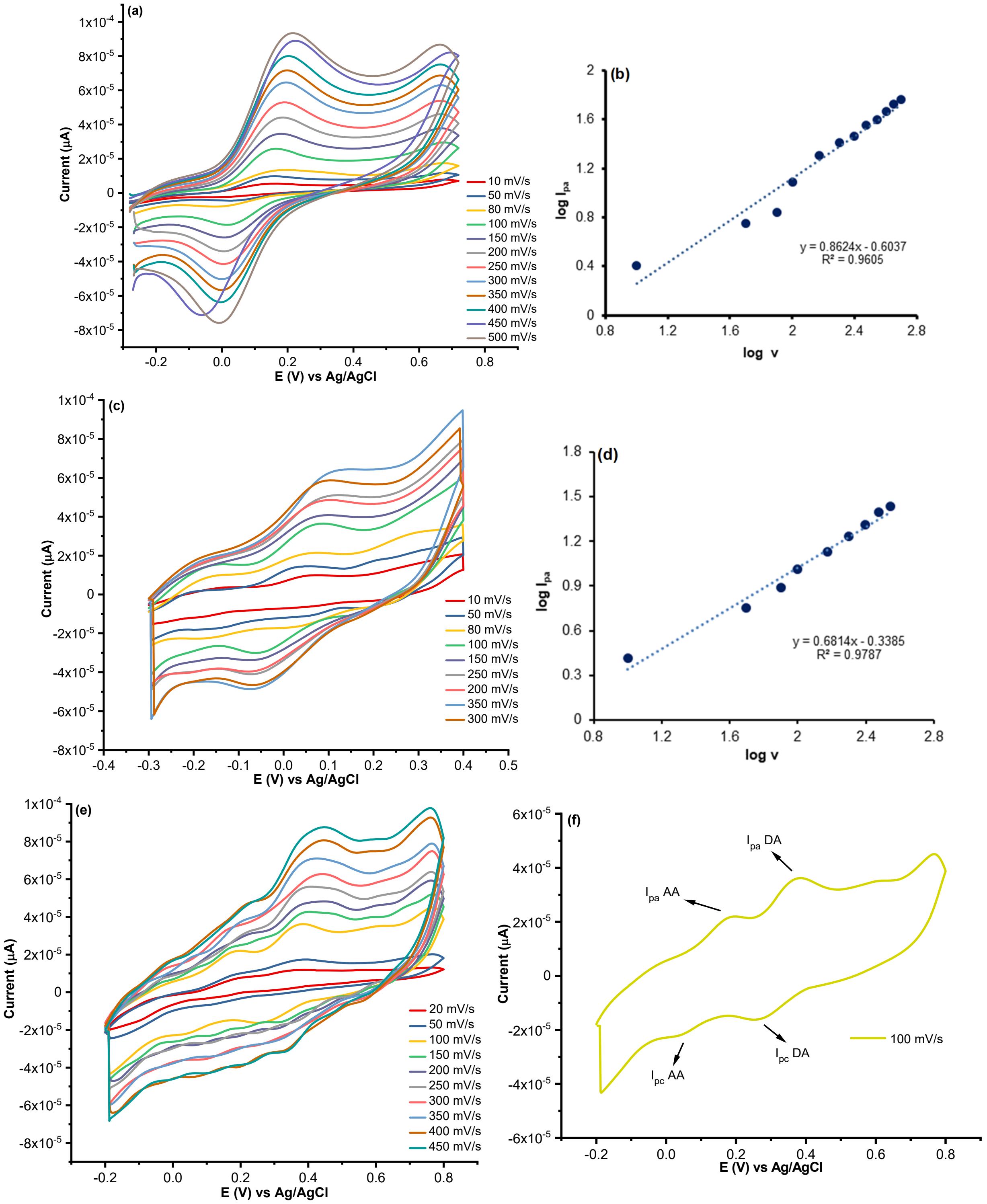


Fig 5. (a) CVs of DA (20 µM) in pH 6 with various scan rates ranging from 10 to 500 mV s^{-1}, (b) plot of log I_{pa} vs log v DA, (c) CVs of AA (20 µM) in pH 7 with various scan rate in ranging from 20 to 450 mV s^{-1}, (d) plot of log I_{pa} vs log v AA CVs of simultaneous DA (20 µM) and (e) AA (20 µM) in pH 3 with various scan rate in ranging from 20 to 450 mV s^{-1} and (f) CVs of simultaneous DA and AA in pH 3 at scan rate 100 mV s^{-1}

and AA was investigated by CV in PBS at the optimum pH with the scan rate of 100 mV s^{-1} (Fig. 6). The I_{pa} and E_{pa} data obtained for the simultaneous determination of DA and AA using different electrodes are summarized in Table 2. As shown in Fig. 6(a) and (b), the anodic peak potential of DA and AA was found to be nearly coincident at 0.20 and 0.10 V, respectively. Hence, it was necessary to identify the individual compound in the simultaneous determination using various electrodes. Fig. 6(c) displayed the voltammetric response of the bare CPE which were overlapping and appeared as small broad peaks. This observation indicated that the electron transfer reaction was slow. However, the peak current of PM/CPE was higher than that of CPE, which was presumably due to the presence of an amine group enabling the interaction between DA and AA [16,41]. In addition, AuNPs/CPE and AuNPs/PM/CPE exhibited significantly higher peak currents, indicating better electrochemical performance. This phenomenon could be associated with the large surface area of AuNPs and their good conductor performance, which in turn acted as a suitable mediator for the electron transfer process [59-60]. As shown in Table 2, in contrast to the bare CPE, PM/CPE, and AuNPs/CPE, the AuNPs/PM/CPE demonstrated the highest value of I_{pa}, the smallest value of E_{pa}, and exhibited two well-defined oxidation peaks.

Table 2. Comparison of I_{pa} and E_{pa} measured using various modified electrodes for the determination of simultaneous DA and AA

Electrode	I_{pa} (μA)		E_{pa} (μA)	
	DA	AA	DA	AA
CPE	2.130	2.481	0.268	0.099
PM/CPE	6.845	3.292	0.263	0.098
AuNPs/CPE	13.933	3.982	0.261	0.096
PM/AuNPs/CPE	18.410	5.899	0.259	0.095

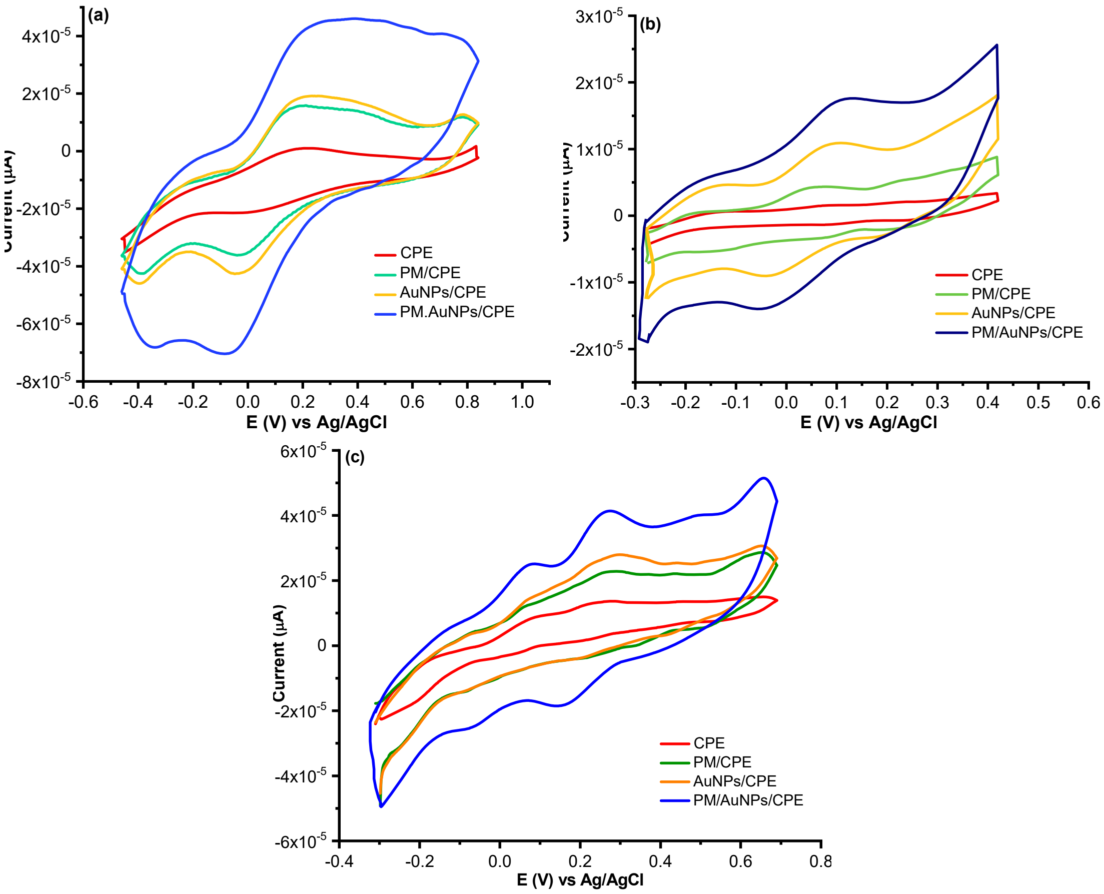


Fig 6. CVs of (a) DA, (b) AA, (c) simultaneous of DA and AA at bare CPE, PM/CPE, AuNPs/CPE, and AuNPs/PM/CPE

The synergy between PM and AuNPs promoted fast electron transfer, and the existence of an amine group selectively facilitated interaction between DA and AA. The AuNPs/PM/CPEs enhanced the catalytic activity 5 and 7 times higher than that of bare CPE in the determination of DA and AA, respectively. The AuNPs/PM/CPE showed a greater potential to separate the anodic peak potential and enhance the sensitivity.

Electrochemical Detection of DA and AA at the Modified Electrodes

Determination of DA and AA using a modified electrode was investigated by LSV under the following optimal conditions: for DA at pH 6 PBS, scan rate of 100 mV s^{-1} with DA concentration range of 0.2–13 μM (Fig. 7(a)) and for AA at pH 7 PBS, scan rate of 100 mV s^{-1} with AA concentration range of 0.4–12 μM (Fig. 8(a)). The curve of DA concentration vs peak current (Fig. 7(b)) presented a good linear relationship with the linear regression equation of I (μA) = 8.830 + 6.472 C (μM, R^2 = 0.9999). Likewise, the oxidation peak current of AA (Fig. 8(b)) is also observed to be linearly proportional to its concentration, with the regression equation of I (μA) = 10.032 + 3.656 C (μA, R^2 = 0.9997). The statistical analyses of DA and AA are summarized in Table 3. The LOD values for DA and AA were estimated to be 0.14 and 0.22 μM, respectively. These results were comparable to those obtained in previous studies, as summarized in Table 4. Moreover, the data indicated that AuNPs/PM/CPE has good sensitivity and can be successfully applied in detecting DA and AA.

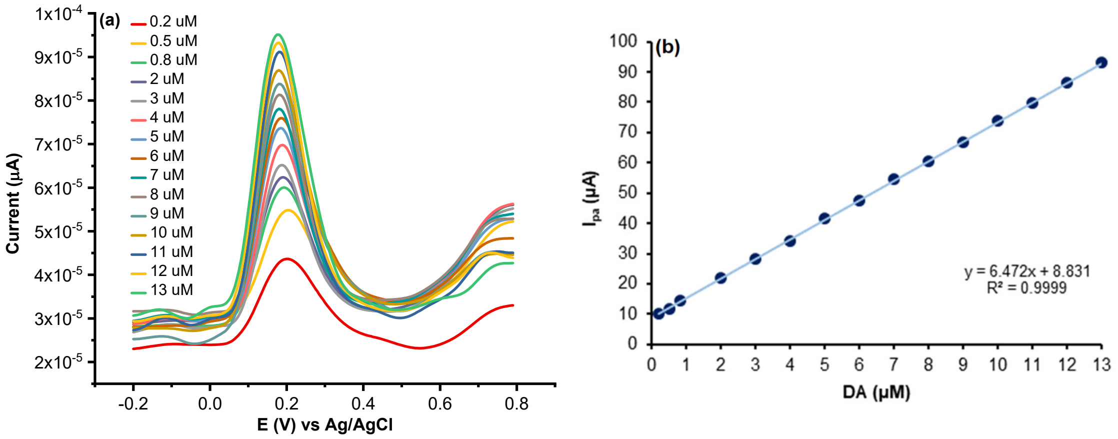


Fig 7. (a) LSVs of DA measured in pH 6 PBS using AuNPs/PM/CPE electrode, with the scan rate of 100 mV s^{-1} and DA concentration range of 0.2–13 μM and (b) the curve of current response I_{pa} vs DA concentration

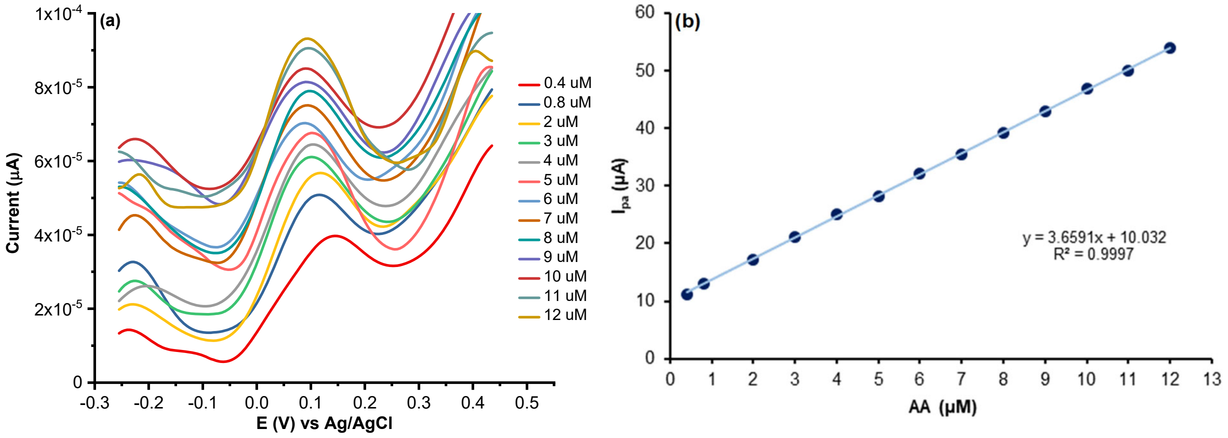


Fig 8. LSVs of AA measured in pH 7 PBS using AuNPs/PM/CPE electrode, with the scan rate of 100 mV s^{-1} and AA concentration range of 0.4–12 μM (a), and the curve of current response I_{pa} vs AA concentration (b)

Determination of Simultaneous DA and AA

The DPV technique was used to further investigate the selectivity of DA and AA using AuNPs/PM/CPE electrodes. The calibration curve for the DPV was constructed by changing the concentration of one species while keeping another constant. Generally, DA and AA have similar peak oxidation potentials, but the AuNPs/PM/CPE electrode could provide a good separation potential peak of the two species (Fig. 9(a)). The electrooxidation of DA becomes another consideration in the simultaneous determination of DA and AA. The presence of AA in the system induced homogeneous catalytic oxidation of AA, which in turn reduced the oxidation of DA [42]. Therefore, it was necessary to eliminate the undesired catalytic oxidation of AA to achieve accurate determination. As shown in Fig. 9,

Table 3. Analytical parameter of DA and AA measurement using AuNPs/PM/CPE electrode

Parameter	DA	AA
pH optimum	6	7
Linear range (µM)	0.2–13	0.4–12
Sensitivity (µA/µM)	6.47	3.66
Limit of detection (µM)	0.14	0.22
Accuration (%)	91.73–106.59	83.63–105.08
Precision (%KV)	0.02–0.66	0.07–0.63

Table 4. Detection limit comparison of DA and AA measurement using the AuNPs/PM/CPE electrode vs the literature values

Electrode material	Detection limit (µM)		Ref
	DA	AA	
Poly(caffeic acid)-modified glassy carbon electrode	0.40	9.00	[50]
Polyglycine-modified CPE	90.00	90.00	[60]
Electrodes modified with self-assembled AuNPs films	0.10	1000.00	[51]
AuNPs@polyaniline core-shell nanocomposites modified electrode	5.00	8.00	[61]
Poly(4-aminobutyric acid) modified glassy carbon electrode	1.00	5.00	[62]
AuNPs/graphene hybrids	0.02	1.00	[63]
Silver nanoparticles/RGO	5.40	1.00	[64]
Nitrogen/graphene	0.25	2.20	[65]
Screen-printed graphene electrode (SPGNE)	0.12	0.95	[66]
Hierarchical nanoporous (HNP)/PtTi	24.00	3.20	[67]
GO/ImAS/GCE	5.00	10.00	[68]
Cis-dioxo-bis[3-methoxy-2,2 dimethylpropanediamine]molybdenum/surfactant	0.40	0.50	[69]
AuNPs/PM/CPE	0.14	0.21	This work

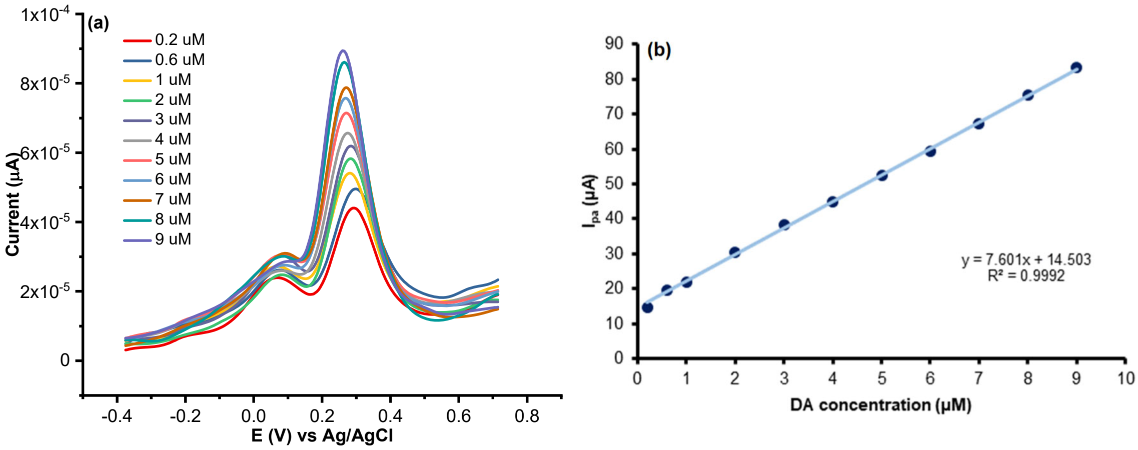


Fig 9. (a) DPVs of 0.1 µM AA and DA with concentration ranging from 0.2–9.0 µM in pH 3 and the scan rate of 100 mV s^{-1} and (b) curve of I_{pa} vs DA concentration

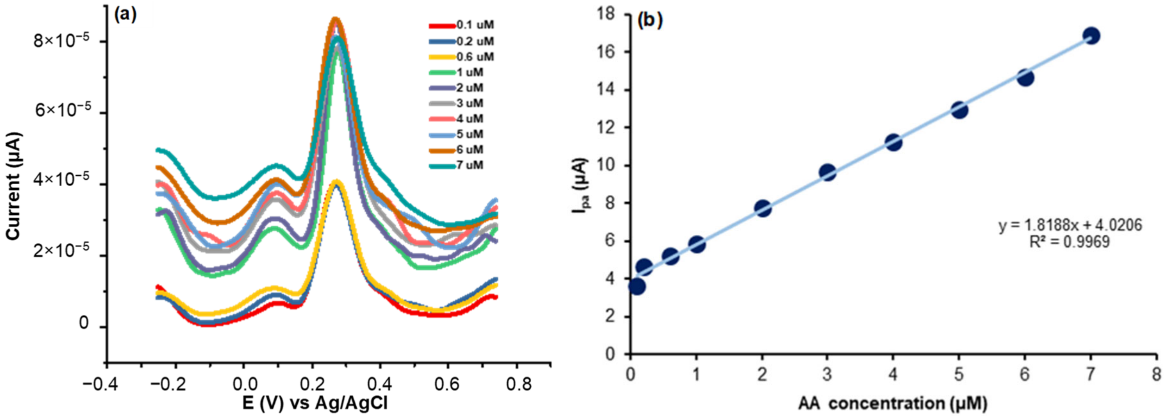


Fig 10. (a) DPVs of 0.1 μM DA and AA with concentration ranging from 0.1–7.0 μM in pH 3 with the scan rate of 100 mV s^{-1}, and (b) curve of I_{pa} vs AA concentration

Table 5. Recovery result of sample spike in real sample using AuNPs/PM/CPE

Sample	Analyte	Concentration added (μM)	Concentration found (μM)	Recovery (%)
Urine	DA	0	-	-
		1	0.9886	98.8600
	AA	0	-	-
		1	0.9828	98.2800

the current response of AA was not significantly affected by the presence of DA in various concentrations. Thus, the use of AuNPs/PM/CPE electrodes could eliminate the homogeneous catalytic oxidation of AA by the oxidized DA. The plot of peak current (I_{pa}) showed a linear relationship with DA concentration with a slope of 7.601 and a correlation coefficient (R^2) of 0.9992 (Fig. 9(b)). A similar experiment was conducted to evaluate the selectivity of AuNPs/PM/CPE for the determination of DA in the presence of AA with various concentrations. Fig. 10(a) displayed the peak potentials of DA and AA, which were well-separated and the anodic peak current increased proportionally with its concentrations. These observations demonstrated that the increase in AA concentration had no influential effect on the detection of DA. The linear regression equation of I_{pa} vs AA concentration is shown in Fig. 10(b), with an R^2 of 0.9969. It was concluded that the AuNPs/PM/CPE electrode could be applied to simultaneously determine DA and AA.

Simultaneous Analysis of DA and AA in Real Sample

The further direction of our research was to evaluate the sensitivity and applicability of modified electrode AuNPs/PM/CPE in determining DA and AA in real samples using the spike method. Firstly, the urine sample was diluted, then spiked with a certain amount of DA and AA and analyzed. The recovery data of the spiked samples are summarized in Table 5. The recovery was observed to sit in the range of 98.28–98.86%. These results indicated that AuNPs/PM/CPE electrodes provided the potential application for sensing DA and AA in the urine sample.

■ CONCLUSION

AuNPs/PM/CPE have been applied for the simultaneous detection of DA and AA. The electrochemical behavior showed that the AuNPs/PM/CPE has a surface area 5 times wider than that of bare electrodes. The AuNPs/PM/CPE electrode presented higher electrocatalytic activity toward the oxidation of DA and AA and could resolve the oxidation peak of the mixture of DA and AA into two well-separated peaks. Furthermore, the AuNPs/PM/CPE electrode showed good linearity, low detection limit, high selectivity, and great potential application for independent and simultaneous measurement of DA and

AA. The AuNPs/PM/CPE electrode has been used to analyze DA and AA in the real samples with satisfying recovery.

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■ AUTHOR CONTRIBUTIONS

Muji Harsini: Conceptualization, Methodology, Resources, Writing – original draft, Visualization. Ainy Nur Farida: Investigation, Resources, Visualization. Erna Fitriany: Methodology, Investigation. Denok Risky Ayu Paramita: Methodology, Investigation. Satya Candra Wibawa Sakti: Methodology, Validation, Visualization. Afaf Baktir: Methodology, Validation, Visualization. Fredy Kurniawan: Methodology, Validation, Visualization. Yudhi Dwi Kurniawan: Writing and editing, Visualization. Bernadeta Ayu Widyaningrum: Conceptualization, Methodology, Validation, Writing – review and editing, Visualization, Supervision. All authors agreed to the final version of this manuscript.

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