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## **Fabrication of Graphene–LaMnO<sub>3</sub> Sensor for Simultaneous Electrochemical Determination of Dopamine and Uric Acid**

**Sedigheh Akbari<sup>1</sup>, Shohreh Jahani<sup>2</sup>, Mohammad Mehdi Foroughi<sup>\*1</sup>, Hadi Hassani Nadiki<sup>1</sup>**

<sup>1</sup>*Department of Chemistry, Kerman Branch, Islamic Azad University, Kerman, Iran*

<sup>2</sup>*Bam University of Medical Sciences, Bam, Iran*

*(Received 14 Feb. 2020; Final revised received 24 May 2020)*

### **Abstract**

Dopamine (DA) and uric acid (UA) are two of important bimolecular widely circulated in body blood. Therefore, development of simple and rapid methods for simultaneous determination of them in routine analysis has a great significance for many researchers. Therefore, for the first time, nanocomposite of graphene (Gr)-LaMnO<sub>3</sub> has been utilized to fabricate the new electro-chemical sensor for simultaneously determining DA and UA via immobilizing Gr-LaMnO<sub>3</sub> on the glassy carbon electrode (GCE). Because of the very good catalytic activities, greater electrical conductivity as well as higher surface area of the Gr-LaMnO<sub>3</sub>, DA and UA with two clearly described peaks have been simultaneously determined at the Gr-LaMnO<sub>3</sub> modified electrode. Relative to peaks at the bare GCE, oxidation currents of DA and UA notably enhanced. Moreover, the catalytic peak current linearly depended on concentration of DA and UA in a range of 0.33 – 283.3 and 0.33 – 283.3 μM with 0.040 and 0.051 μAμM<sup>-1</sup> sensitivity. In addition, limit of detection (LOD) for DA and UA equaled 0.03 and 0.045 μM and diffusion coefficient for DA and UA diffusion at the modified electrode has been computed as 1.71×10<sup>-5</sup> and 1.38×10<sup>-5</sup> cm<sup>2</sup> s<sup>-1</sup>, respectively. It has been found that our electrode could have a successful application for detecting DA and UA in real samples. Thus, this condition demonstrated that the Gr-LaMnO<sub>3</sub> nanocomposite displays good analytical performances to detect DA and UA.

**Keywords:** Nanocomposite of Graphene-LaMnO<sub>3</sub>, Electrochemical sensor, Dopamine, Uric acid.

**\*Corresponding author:** Mohammad Mehdi Foroughi, Department of Chemistry, Kerman Branch, Islamic Azad University, Kerman, Iran. E-mail: mohammadmehdi869@yahoo.com, Tel.: +98 34331321750.

## **Introduction**

Experts in the field largely attracted by graphene (GR) nano-sheets for developing the electro-chemical sensors and bio-sensors, as one of the support materials for improvement in electro-chemical reactivity of the molecules on the modified electrode surface because of its more reasonable features like very good thermal, electrical, mechanical, and optical [1]. Researchers have also synthesized the novel composites of Gr with the inorganic particles like metal, metal hydroxide, metal sulfide, and metal oxide [2-6]. Moreover, electro-chemical sensors, because of the presence of Gr exhibit exceptional improvements in electrical features and utility of inorganic particles for various composites [7]. In addition, authors extensively examined and applied perovskites nano-crystal, as a result of their electrically active structures [8], magnetic [9] and dielectric features [10] as inorganic particles for developing electro-chemical gas sensors [11], solid fuel cells [12], as well as several electro-chemical catalytic procedures [13].

According to the studies, DA and UA have been considered as the two major bio-molecule widely circulated in the body blood and brain with a significant contribution to multiple biological processes in humans' body and brain [14]. In fact, DA has been introduced as one of the crucial neuro-transmitter molecules belonging to the catecholamine that has shown wide circulation in the mammalian central nervous system (CNS) to transfer messages with a key contribution to the function of hormonal, cardio-vascular, and renal systems [15,16]. Actually, DA standard level in the humans' blood ranges between 0.01 and 1  $\mu\text{M}$  and its deficiency indicates numerous diseases like HIV, renal infarction and Parkinson's [17-19].

Moreover, UA has been considered as the end product of the purine degradation metabolism with a normal level in serum ranging between <420  $\mu\text{M}$  in male and 330-360  $\mu\text{M}$  in female [20]. However, abnormal concentration level of UA results in multiple diseases like hyper-uricaemia, gout, leukemia, and pneumonia [21, 22]. It has been shown that DA and UA co-exist in the body fluids. Hence, it is of high prominence to present simplified fast methods to simultaneously determine them in the routine analyses [23,24]. Researchers employed fluorimetry, chemiluminescence, capillary electro-phoresis, ultra violet visible spectroscopy and ion-exchange column chromatography for determining such bio-molecules but these procedures have some complexities, are costly and suffer from low sensitivity, reproducibility and selectivity. Thus, due to the respective benefits, electro-chemical techniques would be the optimal options for overcoming the above problems to determine bio-molecules [25-29].

Nonetheless, one of the major problems in its electro-chemical determination has been shown to be DA and UA interference in each other that co-exist in the biological matrices [30]. However, at the un-modified electrodes like GCE, gold, and platinum, UA and DA may be oxidized in the aqueous

solution at the very close potentials [31,32]. Hence, it would be so hard to have a simultaneous electro-chemical determination of UA and DA. For resolving this problem, experts in the field presented diverse modifiers such as carbon nanotubes (CNTs), nanoparticles (NPs), polymer films, Schiff bases as well as amino acid [33-38].

This is the first study, which dealt with preparing a novel modified, GCE-based on Gr-LaMnO<sub>3</sub> in order to electroanalyze and determine DA and UA. Therefore, voltammetric peaks of DA and UA have been completely described at the developed modified GCE. Analysis indicated lower LOD and higher sensitivity for the above two species because of the increased electro-catalytic features of Gr-LaMnO<sub>3</sub>. Then, voltammetry has been chosen to evaluate analytical function of the sensor for simultaneously determine DA and UA. Functional utilization of this electro-chemical sensor has been verified by simultaneously determining the DA and UA in the humans' urine and blood serum as the real samples.

## **Experimental**

### *Reagents and solutions*

Manganese sulphate, lanthanum chloride and oleic acid were purchased from Merck and used as received. The DA and UA were purchased from Sigma-Aldrich (Sigma-Aldrich, USA,) and used as received. A 0.01M DA and UA solution was prepared daily by dissolving appropriate amount of DA and UA in water and the solution was diluted to 100 mL with distilled deionized water in a 100 mL volumetric flask. The solution was kept in a refrigerator in dark. More dilute solutions were prepared by serial dilution phosphate buffer solutions. Phosphate buffer solution (PBS, 0.1 M) was prepared by mixing the stock solution of 0.1 M NaH<sub>2</sub>PO<sub>4</sub> and 0.1 M Na<sub>2</sub>HPO<sub>4</sub>, and the pH was adjusted by HCl or NaOH. All other materials used were analytical reagent grade and all solutions were prepared with double distilled deionized water. All the chemicals were used without more purification. The nanocomposite of graphene (Gr)-LaMnO<sub>3</sub> was synthesized as described in our previous work [39].

### *Apparatus*

According to the research design, FT-IR spectra have been registered as the KBr disks on a JASCO FT/IR-460 PLUS device. Moreover, X-ray powder diffraction (XRD) has been analyzed on a Philips analytical PC-APD X-ray diffractometer with the graphite mono-chromatic Cu K $\alpha$  radiation ( $\alpha_1$ ,  $\lambda_1=1.54056$  Å,  $\alpha_2$ ,  $\lambda_2=1.54439$  Å) for verifying formation of products. In addition, surface analysis has been performed by a low vacuum JSM, 6380 LV SEM/EDS following the samples' coating with a thin layer of gold (Au) via magnetron sputtering. It is notable that energy-dispersive

X-ray spectrometry (EDX) has been proposed as a key nondestructive analytical tools commonly utilized for chemical composition analysis. Then, electro-chemical determination has been accomplished with an SAMA 500 Electro-analyzer (SAMA Research Center; Iran) that has been controlled by a personal computer. The 3-electro-chemical cell system containing the fluorine-doped tin oxide working electrode (modified, unmodified, GCE), a Pt wire electrode as the auxiliary electrode, and a saturated calomel reference electrode (SCE). Each electro-chemical determination has been conducted in a pure nitrogen atmosphere at the room temperature.

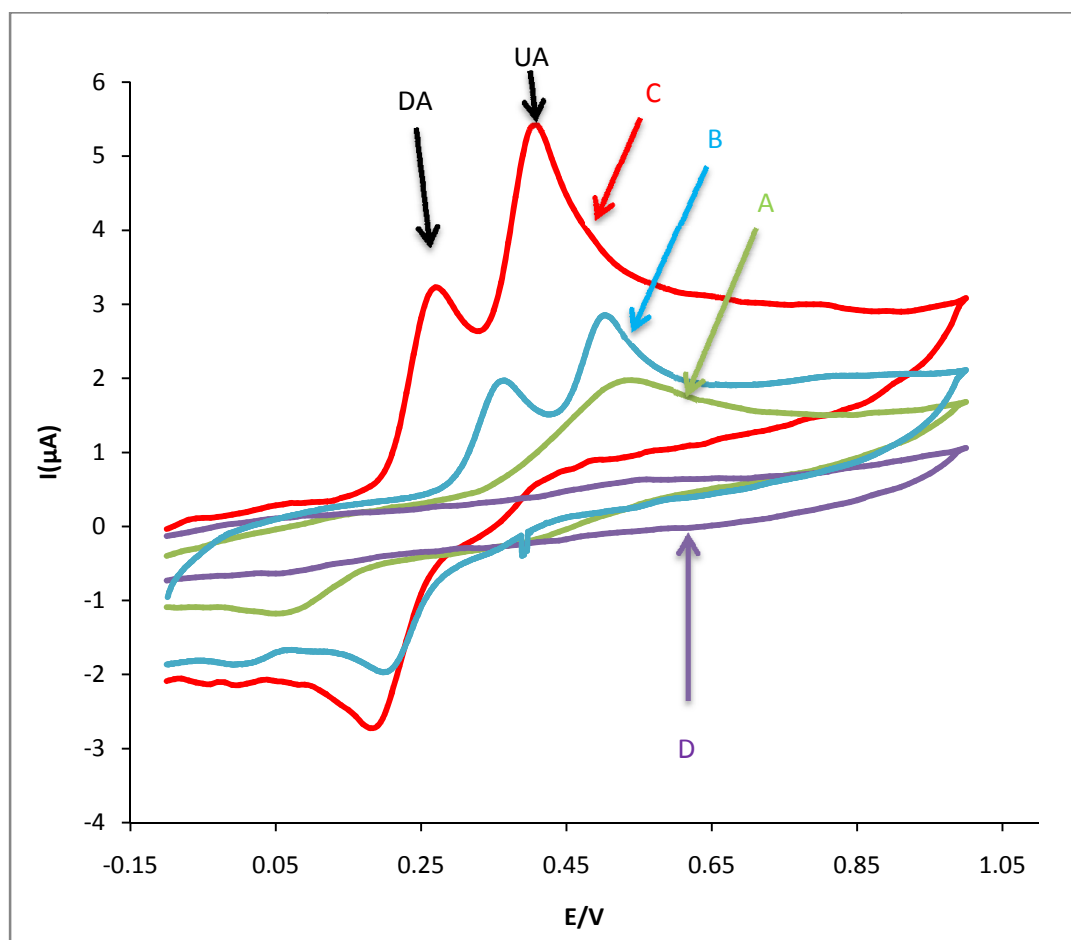
#### *Preparation of the GCE and modified electrode*

Before modifying the surface, we completely polished GCE with 0.3 and 0.05  $\mu\text{m}$  alumina slurry for obtaining a mirror-like surface. Following the sonication in ethanol and water for 20 seconds, we used water to wash the electrode, and consequently dried it below an infrared lamp. Then, GCE/Gr-LaMnO<sub>3</sub> has been procured by casting 4  $\mu\text{L}$  of Gr-LaMnO<sub>3</sub> suspension (0.005 g Gr + 50  $\mu\text{L}$  chitosan 1% + 0.95 mL H<sub>2</sub>O + 0.01 g LaMnO<sub>3</sub>) on the cleaned GCE surface. Afterwards, solvent has been evaporated under the infrared heat lamp. Finally, GCE/Gr and GCE/ LaMnO<sub>3</sub>, as the controls, have been made with the same processes by just replacement of the Gr-LaMnO<sub>3</sub> hybrid materials with LaMnO<sub>3</sub> or Gr.

## **Results and discussion**

### *Voltammetric behaviors of DA and UA*

In this section, cyclic voltammetry (CV) has been used to completely analyze electro-chemical behaviors of the mixed constituents of UA, DA, and XN (66.6 $\mu\text{M}$  each) in 0.1M PBS at pH of 5.0 at the surface of the bare GCE (BGCE), GCE/ LaMnO<sub>3</sub>, GCE/Gr-LaMnO<sub>3</sub>. The BGCE electrodes exhibited a weak broad oxidation peak for DA and UA mixture at 0.52 (Figure 1A), reflecting slower kinetics of electron transfer. Then, oxidation peak of DA and UA was mixed with a very low peak current. On contrary, GCE/ LaMnO<sub>3</sub> modified electrode displayed 2 completely described sharp peaks for DA and UA at 0.348 and 0.49. With regard to Figure 3B, peak current for DA and UA at GCE/LaMnO<sub>3</sub> is many times bigger than unmodified electrode due to the reduced LaMnO<sub>3</sub> film, which acted as a promoter via accelerating the electron transfer. Moreover, the peak potential shifted to a less positive potential in comparison to BGCE. Following the addition of Gr into the modifier composition, the peak current enhanced (Figure 1C), which results from higher surface and conductivity of Gr. Thus, separation of the oxidation peak potential of DA-UA equaled 0.141 V that has been sufficient for simultaneously determines DA and UA.



**Figure 1.** (A) CV at BGC, (B) GCE/LaMnO<sub>3</sub>, (C) GCE/Gr-LaMnO<sub>3</sub> electrodes in the presence of DA and UA (100.0 μM) and (D) as (C) in absence of DA and UA in PBS (0.1 M) at pH 5, scan rate: 100 mV s<sup>-1</sup>.

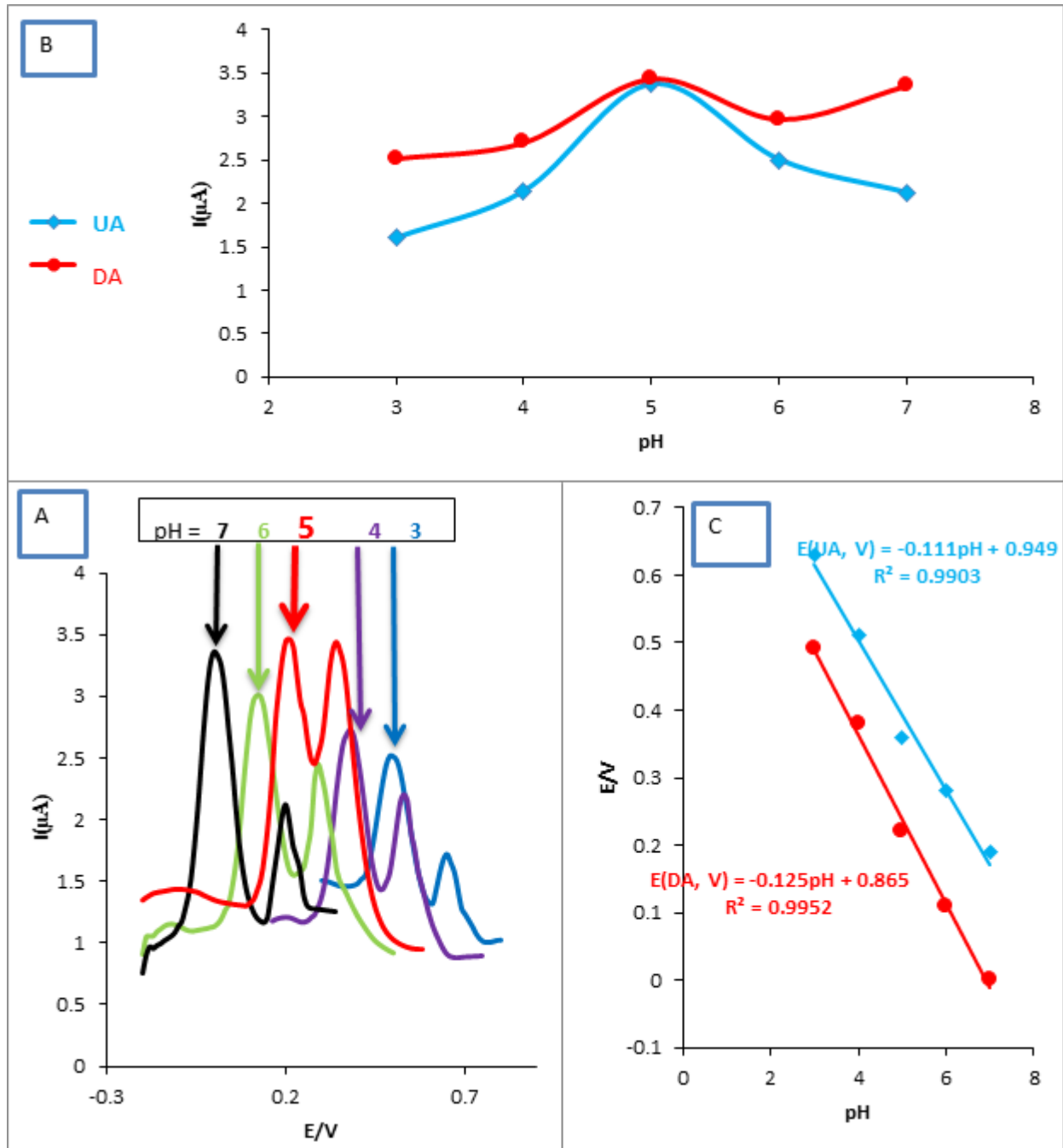
#### *Effect pH on the oxidation of DA and UA*

It is widely accepted that acidity of electrolyte significantly influences DA and UA electro-oxidation because the protons involve in the electrode reaction. Therefore, pH impact on the GCE/Gr-LaMnO<sub>3</sub> signal has been completely examined by CV with 0.1 M PBS at the pH in the ranges between 3 and 7. Figure 2 depicts the outputs. Then, peak current of DA and UA elevated by enhancing pH of solution until it reached 5 and gradually decreased. According to Figure 4B, maximum peak current has been observed at pH of 5 for each compound. When the medium pH slowly enhanced, peak potential DA and UA oxidation shifted toward less positive values, reflecting the contribution of protons to their electrode procedures. It should be mentioned that PBS with a pH of 5 showed the most optimal response for the peak shape and current; therefore, it has been selected as the best pH for additional investigations. Figure 2C displays  $E_p$  versus. pH plot for DA and UA in the working pH range.  $E_p$  of both compounds linearly correlated to the pH of PBS in these equations:

$$\text{DA: } E_p (\text{V}) = -0.125 \text{ pH} + 0.865 \quad (R^2 = 0.9952) \quad (1)$$

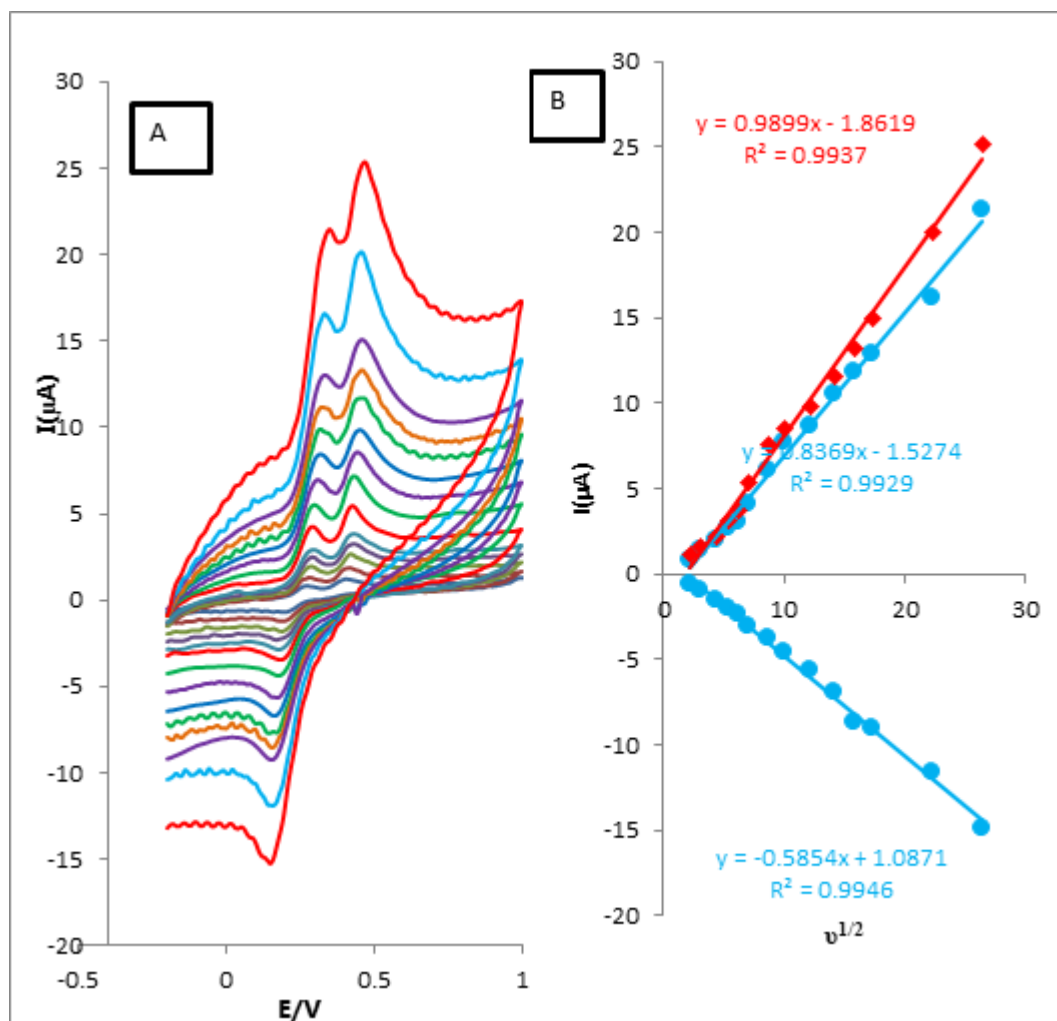
$$\text{UA: } E_p (\text{V}) = -0.111 \text{ pH} + 0.949 \quad (R^2 = 0.9903) \quad (2)$$

With regard to the obtained slopes of 0.125 and 0.111 mV/pH for UA and DA that has been close to the expected Nernstian value for a 2-electron, 2-proton electro-chemical reaction [39]. Consequently, the equal number of the protons and electrons play a role in the electrode reaction.



**Figure 2.** (A) Effect of pH on the peak separation and peak current for the oxidation of DA and UA (66.0 μM); pH= 3-7. Scan rate: 100 mVs<sup>-1</sup>. (B) Plot of peak currents vs pH. (C) Plot of peak potential vs. pH. *Influence of scan rate on the electrochemical behavior of DA and UA.*

In this section, we used CV to examine the impact of the scan rate on oxidation peak current of DA and UA on GCE/Gr-LaMnO<sub>3</sub> modified electrode. With regard to Figure 3A, peak current intensity experienced a continuously elevation by enhancing the scan rate. In addition, there is a direct proportion between current and square root of the scan rate in ranges between 10 and 700 mV s<sup>-1</sup> (Figure 3B), that clearly indicates that redox reaction of DA and UA is a diffusion-controlled procedure. Moreover, peak separation of DA and UA has been satisfactorily performed for analyses at the higher scan rate. Thus, as scan rate elevated, the oxidation peak potential experienced a positive shift, and potential of the reduction peak experienced a negative shift. According to the outputs, at the greater scan rates, a kinetic limitation occurs during the reaction between GCE/Gr-LaMnO<sub>3</sub> composite and DA and UA. Hence, 100 mV s<sup>-1</sup> has been selected as the most optimal scan rate as a result of the greatest efficiency obtained in this research for peak separation and currents.



**Figure 3.** (a) CVs of GCE/Gr-LaMnO<sub>3</sub> electrode in pH 5 in the presence of DA and UA (66.0 μM) at various scan rates (from inner to outer curve): 5, 10, 20, 30, 40, 50, 75, 100, 150, 200, 250, 300, 500, and 700 mV s<sup>-1</sup>. (b) The plot of peak currents vs.  $v^{1/2}$ .

*Chronoamperometric study*

Chronoamperometric measurements of DA and UA at GCE/Gr-LaMnO<sub>3</sub> were also studied by setting the working electrode potential at 0.35 and 0.49 V vs. SCE for the various concentration of DA and UA in PBS (pH 5) (Chronoamperogram for DA was shown in Figure 4A and D). For an electroactive with a diffusion coefficient of  $D$ , the current for the electrochemical reaction with a mass transport limited rate is described by the Cottrell equation [39].

$$I = nFAD^{1/2}C_b\pi^{-1/2}t^{-1/2} \quad (4)$$

Under diffusion control, a plot of  $I$  vs.  $t^{-1/2}$  will be linear, and the slope of the linear region of the Cottrell's plot can be used to calculate of the  $D$  for DA and UA. The value of  $D_{DA}$ , and  $D_{UA}$  were found to be  $2.59 \times 10^{-5}$  and  $2.38 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ , respectively. Chronoamperometry was also used for calculation of the catalytic rate constant,  $k$ , for the reaction between DA and UA and the GCE/Gr-LaMnO<sub>3</sub> according to the method of Galus [40]:

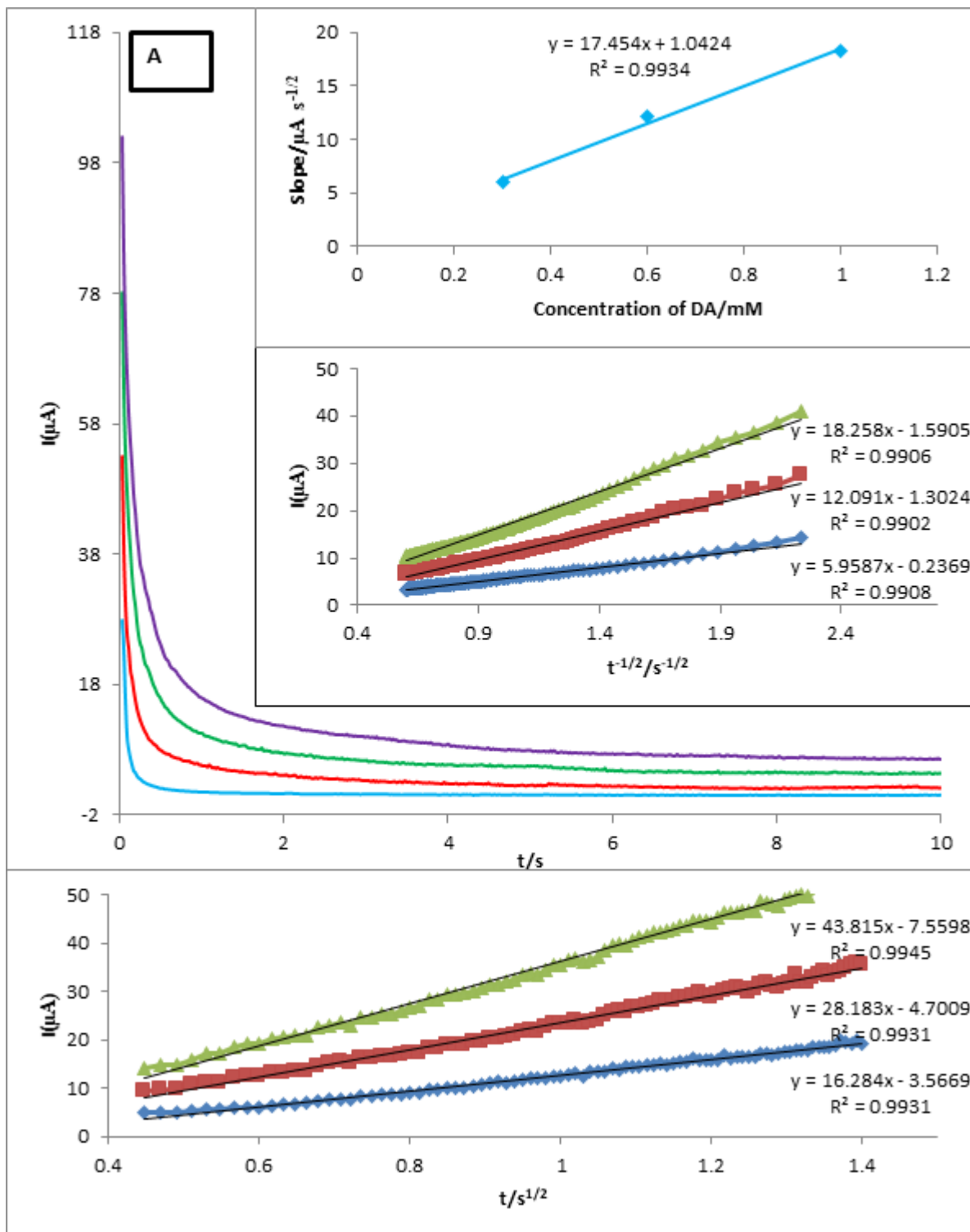
$$\frac{I_C}{I_L} = \gamma^{1/2} \left[ \frac{P^{1/2} \operatorname{erf}(\gamma^{1/2}) + \exp(-\gamma)}{\gamma^{1/2}} \right] \quad (5)$$

Where  $I_C$  is the catalytic current of DA and UA at the GCE/Gr-LaMnO<sub>3</sub>,  $I_L$  is the limiting current in the absence of DA and UA and  $\gamma = kC_b t$  is the bulk concentration of DA and UA is the argument of the error function. In the cases where  $\gamma \gg 1$  the error function exceed is almost equal to 1 and consequently the above equation can be reduced to:

$$\frac{I_C}{I_L} = \pi^{1/2} \gamma^{1/2} = \pi^{1/2} (kC_b t)^{1/2} \quad (6)$$

Where  $t$  is the time elapsed in seconds. Based on the above equation, the slope of the  $I_C/I_L$  vs.  $t^{1/2}$  plot can be used to calculate the rate constant of the catalytic process  $k$  for a given DA and UA concentration. Such plots achieved from the chronoamperograms in Figure 4A are shown in Figure 4D. From the values of the slopes an average value of  $k$  was found to be  $k = 4.39 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$  for DA. Also  $k = 1.21 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$  was calculated for UA. The value of  $k$  explains as well as the sharp feature of the catalytic peak observed for catalytic oxidation of DA and UA at the surface of GCE/Gr-LaMnO<sub>3</sub>.

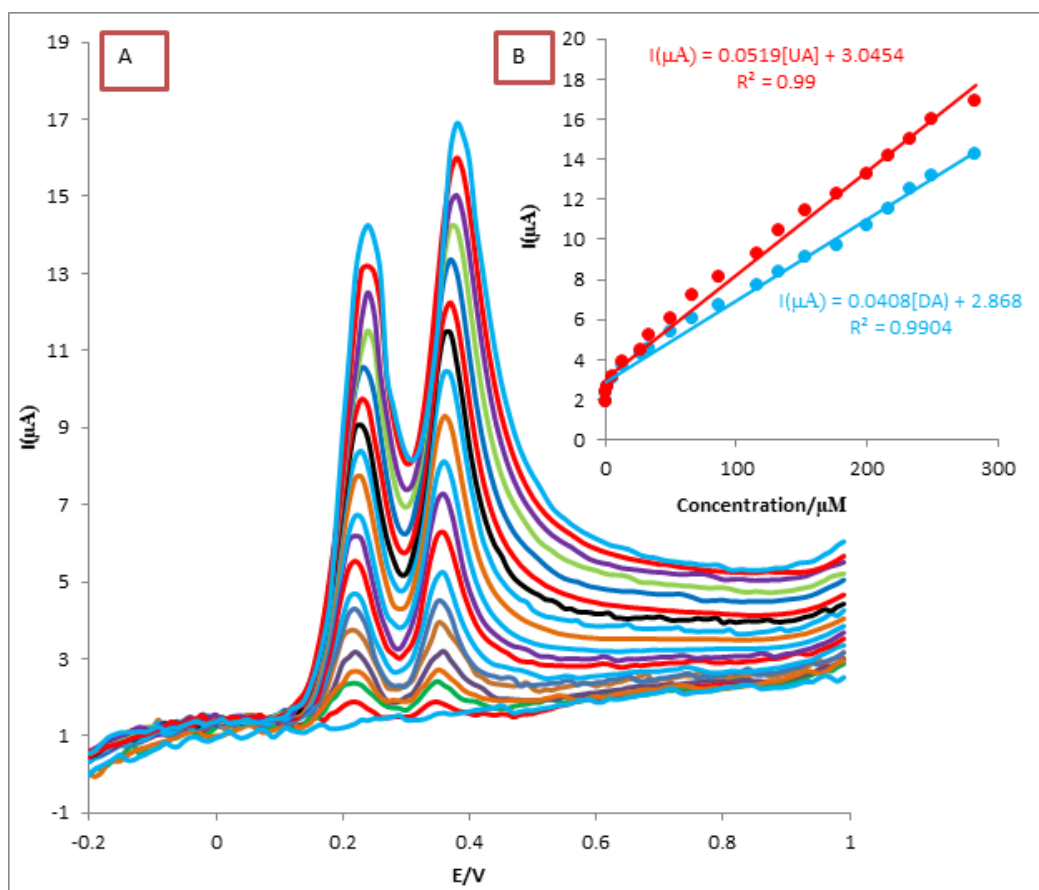




**Figure 4.**(A) Chronoamperograms obtained at GCE/Gr-LaMnO<sub>3</sub> in 0.1 M PBS (pH 5.0) for different concentration of DA. The numbers 1–4 correspond to: 0.0, 0.3, 0.6 and 1.0 mM of DA. Insets: (B) Plots of  $I$  vs.  $t^{-1/2}$  obtained from chronoamperograms 1–4. (C) Plot of the slope of the straight lines against DA concentration. (D) Plots of  $I_C/I_L$  vs.  $t^{1/2}$  obtained from chronoamperograms 1–4.

*Simultaneous determination of DA and UA*

Studies confirmed coexistence of DA and UA in the humans' body fluids. Based on the clinical perspectives; it is of high importance to determine DA and UA simultaneously. In this regard, DPV has been used for determining the association of the peak current with DA and UA concentration. According to Figure 5, two completely defined oxidation peaks have been observed on the DPV curves. Figure 5B showed linear dependence of electro-catalytic peak current of DA and UA oxidation at GCE/Gr-LaMnO<sub>3</sub> surface on the DA and UA concentration in ranges between 0.33 and 283.3  $\mu\text{M}$  with a LOD equal to 0.04 and 0.051  $\mu\text{A}\mu\text{M}^{-1}$ . Moreover, for 7 consecutive determinations of 66.6  $\mu\text{M}$  of UA and DA, the relative standard deviation equaled 2.1% and 1.8%. Therefore, outputs showed the effective utilization of the new electrode to simultaneously determine DA and UA.



**Figure 5.** (A) DPV of the mixtures of, DA and UA at the GCE/Gr-LaMnO<sub>3</sub> electrode in PBS (pH 5) at the scan rate of 100  $\text{mV s}^{-1}$ . Concentrations from inner to outer of curves: DA and UA (0.0, 0.33, 0.9, 2.3, 5.0, 6.6, 13.3, 26.6, 33.3, 50.0, 66.06, 86.6, 116.0, 133.3, 153.3, 176.6, 200.0, 216.6, 233.3, 266.6 and 283.0) Insets: (b) and (c) Plots of I vs. Concentrations.

This value is comparable with values reported by other research groups for simultaneous electro-oxidation of DA and UA at the surface of chemically modified electrodes by other modifiers (see Table 1).

**Table 1.** Comparison of the efficiency of some modified electrodes used in the electro-oxidation of DA and UA.

Electrode	Modifier	Method	LOD ( $\mu\text{M}$ )		LDR ( $\mu\text{M}$ )		Ref.
			DA	UA	DA	UA	
Glassy carbon	Copper (II) oxide nano-rice	Voltammetry	0.42	1.2	1.0-150.0	1.0-160.0	[41]
Screen-printed carbon	Gold-decorated-polydopaminenanospheres	Voltammetry	$1.0 \times 10^{-3}$	$1.0 \times 10^{-3}$	1.0-350.0	1.0-280.0	[42]
Glassy carbon	Chitosan/glucose oxidase/Prussian blue-graphite	Voltammetry	0.08	0.11	0.1-80.0	0.2-30.0	[43]
Screen-printed carbon	Graphene oxide/silver nanowires/silver nanoparticles	Voltammetry	0.16	0.58	0.6-50.0	1.0-100.0	[44]
Screen-printed carbon	Graphene quantum dots and ionic liquid	Voltammetry	0.06	0.03	0.2-10.0	0.5-20.0	[45]
Glassy carbon	Gr-LaMnO <sub>3</sub> nanocomposite	Voltammetry	0.04	0.051	0.33-283.3	0.33-283.3	This Work

### Real Sample analysis

According to the research design, humans' serum and urine serum samples have been experimented for evaluating reliability and feasibility of the method presented to determine DA and UA simultaneously. Therefore, content of DA and UA in the serum and urine samples have been determined and the method reliability has been verified by analyzing the samples spiked with certain content of DA and UA. Table 2 presents the results. Analysis indicated recoveries of 95.4 to 102.5% for DA and UA. Finally, the new electrode ability to simultaneously determine DA and UA has been demonstrated.

**Table 2.** Determination of DA and UA in human blood serum and urine samples using GCE/Gr-LaMnO<sub>3</sub> (n = 5).

Sample	Analyte	Detected (μM)	Added (μM)	Found (μM) <sup>a</sup>	Recovery (%)
Human Blood Serum	DA	ND <sup>b</sup>	10.0	9.9±2.6	99.0
			20.0	20.2±3.1	101.0
	UA	ND <sup>b</sup>	5.0	4.9±2.9	98.0
			15.0	14.9±2.3	99.6
Urine	DA	ND <sup>b</sup>	15.0	15.2±1.8	101.3
			25.0	24.7±2.9	98.8
	UA	ND <sup>b</sup>	7.5	7.7±2.4	102.6
			17.5	17.7±1.6	101.1

<sup>a</sup>Mean±standard deviation for n = 5.<sup>b</sup>Not detected

## Conclusions

This is the first research demonstrating one of the efficient approaches for constructing GCE/Gr-LaMnO<sub>3</sub> sensor and its utilization for simultaneously determining UA and DA. In comparison to bare GCE, we found a big peak-to-peak separation between UA and DA as well as considerable enhancement in the peak currents at GCE/Gr-LaMnO<sub>3</sub> that certainly verified the probable use of Gr-LaMnO<sub>3</sub> as one of the effective promoters for enhancing the kinetic of electro-chemical procedure of UA and DA. This new technique had a successful utilization as an electro-chemical sensor to simultaneous determination of DA and UA with a very low detection limit. Additionally, this new sensor has been substantially employed to determine UA and DA simultaneously in the serum and urine samples with acceptable outputs.

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