

Ti₃C₂ Nano Layer Modified Screen Printed Electrode as a Highly Sensitive Electrochemical Sensor for the Simultaneous Determination of Dopamine and Tyrosine

Navid Arbabi^{a, *} and Hadi Beitollahi^{b, **}

^a Department of Chemistry, Graduate University of Advanced Technology, Kerman, 7631818356 Iran

^b Environment Department, Institute of Science and High Technology and Environmental Sciences, Graduate University of Advanced Technology, Kerman, 7631818356 Iran

*e-mail: arbabi1370@gmail.com

**e-mail: h.beitollahi@yahoo.com

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Abstract—A highly sensitive method is proposed for the simultaneous determination of dopamine and tyrosine using a Ti₃C₂ nano layer modified screen printed electrode. The electro-oxidation of dopamine at the surface of the modified electrode was studied using cyclic voltammetry, chrono-amperometry, and differential pulse voltammetry. Under the optimized conditions, the differential pulse voltammetric peak current of dopamine increased linearly with dopamine concentrations in the ranges of 0.5–600.0 μM, and the detection limit of 0.15 μM was obtained for dopamine.

Keywords: dopamine, tyrosine, Ti₃C₂ nano layer, modified electrode

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INTRODUCTION

Dopamine (DA) and tyrosine (Tyr) are well known as an extracellular chemical messenger called neurotransmitter (NTM) and an essential amino acid in biological systems, respectively. DA plays an important physiological role in the functioning of central nervous, renal, hormonal, and cardiovascular systems as an NTM [1–4], and it is an immune regulator under septic conditions [5]. The loss of an NTM may result in some serious diseases, such as Parkinson's disease and schizophrenia [6, 7].

Tyr is a vital constituent of proteins, which is indispensable in human nutrition for establishing and maintaining a positive nitrogen balance [8]. Addition of Tyr to dietary and food products or pharmaceuticals is sometimes necessary due to its scarcity in some food materials. Trace-levels of Tyr can modulate and control acetylcholine receptors metabolic stability in muscle cells [9]. A high concentration of Tyr in a culture medium results in an increased sister chromatid exchange, while the absence of Tyr could lead to the impairing of protein synthesis, thus it causes development of imbalance in biological systems. In pharmaceutical industry, Tyr can be converted to DA using enzymatic reaction. To control the reaction progress, a sensor may be needed to obtain the necessary

amounts of the end product (DA) and of the substrate (Tyr).

Thus, various commonly usable analytical methods for DA and Tyr have been developed. Some examples of these methods are the ultrahigh performance liquid chromatography tandem mass spectrometry [10], chemiluminescence [11], spectroscopy [12], and spectrofluorimetry [13].

All these techniques, however, require a compressing system, temperature controlling systems, separation systems, and other spectro-photometric or electric detection systems. The electrochemical methods have received special attention due to their unique qualities such as a simple pretreatment procedure, less time-consumption, better selectivity, good sensitivity, and low cost [14–21]. In this sense, electrochemical detection of DA and Tyr has received much interest due to their importance for the central nervous system. However, a significant problem for DA and Tyr determination is the fouling effect due to the accumulation of reaction products on the electrode surface [22]. Thus, a promising approach to overcome problems arising from fouling of the biological substrate is the use of chemically modified electrodes [23–30]. Recently, MXenes (of the formula M_{n+1}X_nT_x, where M is a transition metal, X is C and/or N, and T_x denotes –OH, –F, and =O surface groups), a novel

family of two-dimensional metal carbides, have been used which can be produced by the selective etching of the A-group (generally group IIIA and IVA elements) layers from the MAX phases [31–33]. MXenes have already demonstrated their potential as promising electrode materials for Li-ion batteries [34], supercapacitors [35], and sensors [36, 37] because of their high electrical conductivity, a large surface area, a layered structure, remarkable chemical stability, and environmentally friendly characteristics [38, 39].

A screen-printed electrode (SPE) is an attractive alternative choice due to its miniaturized size, low cost, easiness in fabrication, rapid responses, and disposability, which makes it especially suitable for an on-site analysis [40–45].

In this study, a highly sensitive electrochemical method for the simultaneous determination of DA and Tyr using Ti_3C_2 modified SPE (Ti_3C_2/SPE) is reported. The proposed method is simple, sensitive, easy, and economical for a routine analysis. The authors consider that the proposed method would be a potential step forward in the simultaneous electrochemical determination of DA and Tyr in biological fluids.

EXPERIMENTAL

Apparatus and Chemicals

The electrochemical measurements were performed with an Autolab potentiostat/galvanostat (PGSTAT 302N, Eco Chemie, the Netherlands). The experimental conditions were controlled with the General Purpose Electrochemical System software. The SPE used (Drop Sens, Oviedo, Spain) consisted of three main parts: a graphite counter electrode, a silver pseudo-reference electrode, and a graphite working electrode.

All solutions were freshly prepared with double distilled water. DA, Tyr, and all of the other reagents were of the analytical grade and were used as obtained from Merck (Darmstadt, Germany). The buffer solutions (PBSs) were prepared from orthophosphoric acid and its salts in the pH range of 2.0–9.0.

Synthesis of Ti_3C_2 Nano Layers

In the first step, titanium powder, aluminum powder, and graphite powder with molar ratios of 3, 1.1, and 1.9 were injected into a pellet mill over a period of 360 min, at 600 rpm to synthesize the nano layers. MXene layers were inserted, and MXene was prepared in the powder form with Ti_3AlC_2 formula.

Next, 60 mL of 40% purity hydrogen fluoride solution was added to 0.2 g of Ti_3AlC_2 powder and heated at 25°C for 20 h. Afterwards, to prepare MXene with Ti_3C_2 formula, the prepared suspension was centri-

fuged and washed with deionized water, and the precipitate was dried at 55°C [46].

Preparation of Modified Electrode

To prepare Ti_3C_2/SPE a bare SPE was coated with Ti_3C_2 nano layers as follows: 1 mg of Ti_3C_2 nano layers was dispersed in 1 mL distilled water and ultrasonicated for about 30 min. Next, 5 μ L of this suspension was coated on the surface of the SPE and dried at room temperature.

Preparation of Real Samples

One milliliter of DA from an ampoule was diluted to get 10 mL with 0.1 M PBS (pH 7.0); then, different volumes of the diluted solution were transferred into each of a series of 25 mL volumetric flasks and diluted to the mark with PBS. The DA content was analyzed by the proposed method using the standard addition method.

Urine samples were stored in a refrigerator immediately after collection. Ten milliliters of the samples were centrifuged for 15 min at 2000 rpm. The supernatant was filtered out by using a 0.45 μ m filter. Next, different volumes of the solution were transferred into a 25 mL volumetric flask and diluted to the mark with PBS (pH 7.0). The diluted urine samples were spiked with different amounts of DA and Tyr. The DA and Tyr contents were analyzed by the proposed method by using the standard addition method.

RESULTS AND DISCUSSION

Electrochemical Behavior of DA on Ti_3C_2/SPE

Due to the fact that the electrochemical behavior of DA is pH-dependent, optimizing the pH of the solution is necessary for obtaining the best results. Hence, the evaluations were performed at different pH values ranging from 2.0–9.0, and the results showed that the best results during the electro-oxidation of DA at the surface of the modified electrodes could be obtained at pH 7.0.

Figure 1 illustrates the cyclic voltammograms (CV) of a 700.0 μ M DA using the Ti_3C_2/SPE (curve *a*) and an unmodified SPE (curve *b*). As it can be easily noticed, the maximum oxidation of DA occurs at 210 mV in the case of Ti_3C_2/SPE , which is around 60 mV more negative than that observed in the case of the unmodified SPE. The peak currents are also much higher in the case of the analyses performed with Ti_3C_2/SPE , thus indicating that the modification of the SPEs with Ti_3C_2 nano layers greatly enhances the

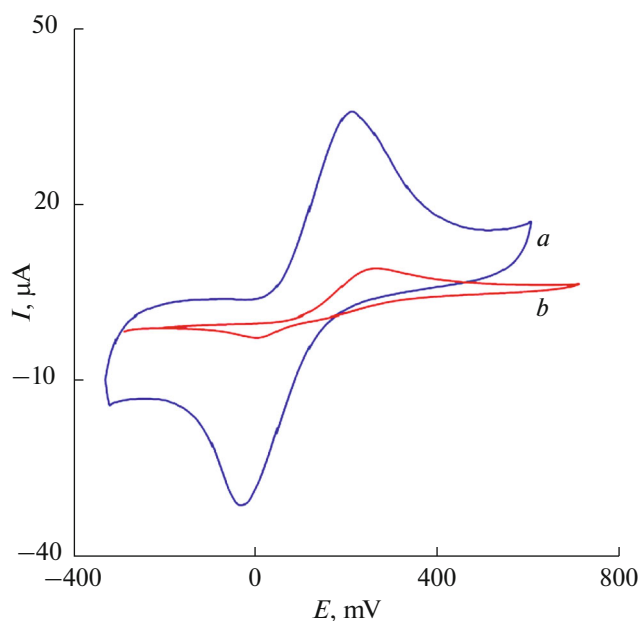


Fig. 1. CVs of: (a) Ti₃C₂ nano layers/SPE, and (b) unmodified SPE in the presence of 700.0 μM of DA at pH 7.0.

electrochemical behaviour of the electrode for the analysis of DA.

Effect of Scan Rate

Increasing the scan rate leads to enhanced oxidation peak currents according to the obtained results from the study of the effect of potential scan rates on the oxidation currents of DA (Fig. 2). In addition, there is a linear relationship between I_p and the square root of the potential scan rate ($v^{1/2}$), which demon-

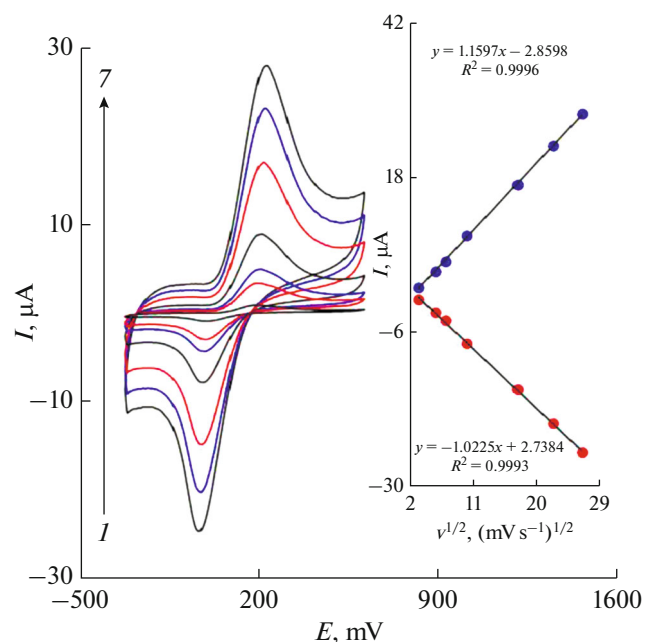
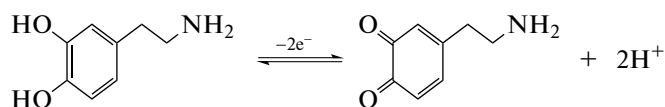


Fig. 2. CVs of Ti₃C₂/SPE in 0.1 M PBS (pH 7.0) containing 50.0 μM of DA at various scan rates. Numbers 1–7 correspond to 10, 30, 50, 100, 300, 500, and 700 mV s⁻¹. Inset: Variations of anodic and cathodic peak currents vs. square root of scan rate.

strates that the oxidation procedure of the analyst is in control of diffusion [47].

The oxidation process of DA is related to the conversion of the catechol group in DA into o-quinone. The electrochemical oxidization process of DA follows the two-electron/two-proton mechanism. The reaction mechanism of DA on the modified electrode surface is in Scheme 1.



Scheme 1. Possible reaction of DA on the electrode.

Chronoamperometric Measurements

Chronoamperometric measurements of DA at Ti₃C₂/SPE were carried out by setting the working electrode potential at 0.25 V for the various concentrations of DA in PBS (pH 7.0) (Fig. 3). For chronoamperometric analysis of electroactive materials under mass transfer limited conditions, the Cottrell equation was used as borrowed from [47]:

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

where D is the diffusion coefficient (cm² s⁻¹), and C_b is the bulk concentration (mol cm⁻³). The best fitting of I

vs. $t^{-1/2}$ plots based on the experimental was found for different DA samples, and the slopes of the straight lines were next plotted against the concentrations of DA. Using the resulting slope and the Cottrell equation, the mean value of D was found to be 2.9×10^{-5} cm²/s.

Calibration Curve

Based on the resulting peak currents of DA when using Ti₃C₂ nano layers/SPE, the quantitative analysis of DA was done in water solutions. The Ti₃C₂/SPE, as working electrode, was used in a range of DA concentrations in 0.1 M PBS via differential pulse voltamme-

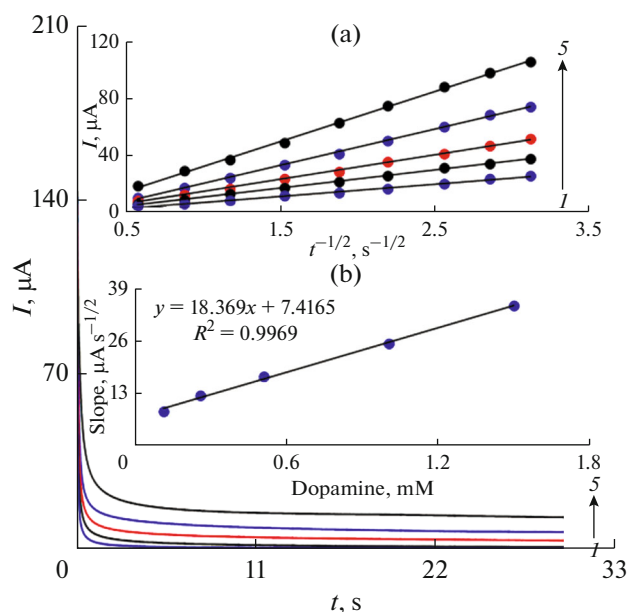


Fig. 3. Chronoamperograms obtained at $\text{Ti}_3\text{C}_2/\text{SPE}$ in 0.1 M PBS (pH 7.0) for different concentrations of DA. Numbers 1–5 correspond to 0.1, 0.25, 0.5, 1.0, and 1.5 mM of DA. Insets: (a) Plots of I vs. $t^{-1/2}$ obtained from chronoamperograms 1–5 and (b) Plot of the slope of the straight lines against DA concentrations.

try (DPV) due to the advantages of DPV including the improved sensitivity and better performance in analytical applications (Fig. 4). According to the results, there is a linear relationship between the peak currents and concentrations of DA within the concentration range of 0.5–600.0 μM , with the correlation coefficient of 0.9992. The detection limit was obtained to be 0.15 μM . Table 1 presents a comparison of $\text{Ti}_3\text{C}_2/\text{SPE}$ analytical performance of this work with other electrochemical sensors involved in the DA analysis studied elsewhere [48–51]. As can be seen, the obtained here results are comparable with those reported by others.

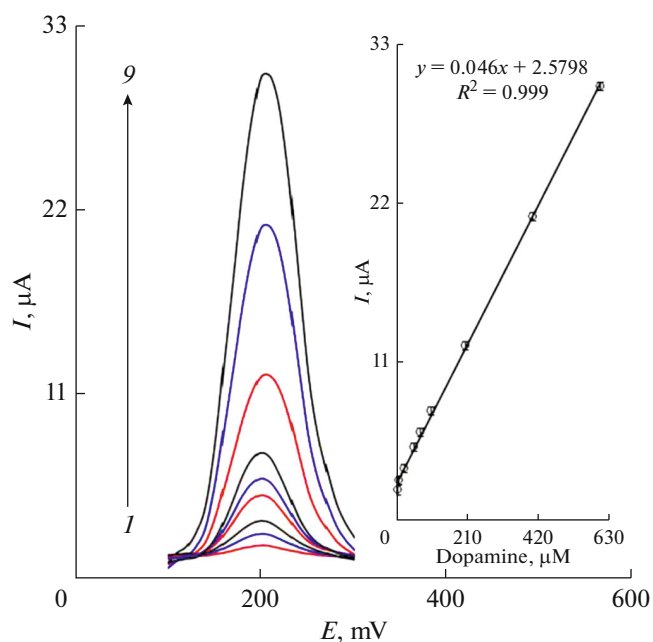


Fig. 4. DPVs of $\text{Ti}_3\text{C}_2/\text{SPE}$ in 0.1M (pH 7.0) containing different concentrations of DA. Numbers 1–9 correspond to 0.5, 5.0, 20.0, 50.0, 70.0, 100.0, 200.0, 400.0, and 600.0 μM . Inset: Plot of the electrocatalytic peak current as a function of DA concentrations in a range of 0.5–600.0 μM .

Simultaneous Determination of Dopamine and Tyrosine

To the best of the authors' knowledge, there is on the modified $\text{Ti}_3\text{C}_2/\text{SPE}$ for the simultaneous determination of DA and Tyr, and this is the first report on this theme.

The electrochemical determination of DA using bare electrodes suffers from the interference by Tyr, because the oxidation potential for Tyr is fairly close to that of DA. The determination of those two compounds was performed by simultaneously changing the concentrations of DA and Tyr, and recording the

Table 1. Comparison of the efficiency of some modified electrodes used in the determination of DA

Electrode	Modifier	Method	Linear range, μM	Detection limit, μM	Ref.
Glassy carbon	$\text{MoS}_2/\text{poly}(3,4\text{-ethylenedioxythiophene})$	DPV	80.0–1.0	0.52	[48]
Carbon fiber	Reduced GO	DPV	224.82–1.5	0.77	[49]
Glassy carbon	l-Tyr covalently functionalized GO composite	DPV	500.0–1.0	0.28	[50]
Gold	Reduced GO- Mn_3O_4 /Nafion-Au	Amperometry	1450.0–1.0	0.25	[51]
Screen printed	Ti_3C_2 nano layers	DPV	600.0–0.5	0.15	This work

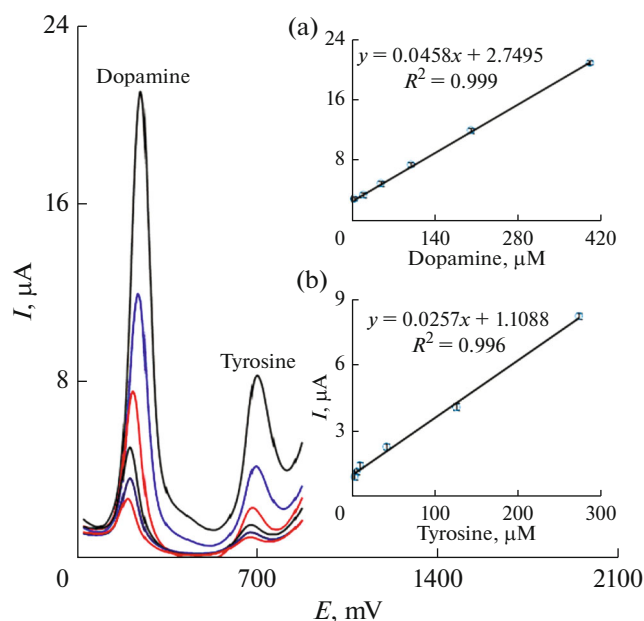


Fig. 5. DPVs of Ti₃C₂/SPE in 0.1M PBS (pH 7.0) containing different concentrations of DA and Tyr: (from inner to outer) mixed solutions of 5.0 + 0.5, 20.0 + 3.0, 50.0 + 7.5, 100.0 + 40.0, 200.0 + 125.0, and 400.0 + 275.0, respectively, in which the first value is concentration of DA in micromolar, and the second value is concentration of Tyr in micro molar. (a) Plot of peak currents as a function of DA concentrations, and (b) plot of the peak currents as a function of Tyr concentrations.

DPV data (Fig. 5). The voltammetric results showed well-defined anodic peaks at potentials of 200 and 700 mV, corresponding to the oxidation of DA and Tyr, respectively, indicating that the simultaneous determination of these compounds is feasible at the Ti₃C₂ nano layers/SPE as shown in Fig. 5. The sensitivity of the modified electrode towards the oxidation of DA was found to be 0.0458 $\mu\text{A } \mu\text{M}^{-1}$. This is very close to the

value obtained in the absence of Tyr (0.046 $\mu\text{A } \mu\text{M}^{-1}$, see Fig. 4), indicating that the oxidation processes of these compounds at Ti₃C₂/SPE are independent, and, therefore, the simultaneous determination of their mixtures is possible without significant interferences.

Analysis of Real Samples

To assess the applicability of the application of the modified electrode for the determination of DA and Tyr in real samples, the described method was applied in DA ampoule and urine samples. For the purpose of the analysis the standard addition method was used, and the results are given in Table 2. The observed recoveries of DA and Tyr were satisfactory, and the reproducibility of the results was demonstrated based on the mean relative standard deviation (R.S.D.).

CONCLUSIONS

This work reports the construction of Ti₃C₂/SPE and its application in the simultaneous determination of DA and Tyr. The modified electrode exhibited excellent electrocatalytic activity towards the detection of DA and Tyr co-oxidized at the electrode with a wide potential difference. Thus, the electrode could electrochemically discriminate the sensing of DA and Tyr. To sum up, simultaneous as well as independent electrochemical determinations of DA and Tyr are possible without electrochemical interference from each other.

CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

Table 2. Determination of DA and Tyr in real samples. All concentrations are in μM ($n = 5$)

Sample	Spiked		Found		Recovery, %		R.S.D, %	
	DA	Tyr	DA	Tyr	DA	Tyr	DA	Tyr
DA tablet	0	0	5.0	—	—	—	3.0	—
	1.0	5.0	6.1	4.9	101.7	98.0	2.4	3.5
	2.0	7.0	6.8	7.2	97.1	102.9	1.9	2.0
	3.0	9.0	8.3	8.8	103.7	97.8	2.7	2.4
	4.0	11.0	8.9	11.1	98.9	100.9	2.3	1.8
Urine	0	0	—	—	—	—	—	—
	5.0	4.0	4.9	4.1	98.0	102.5	1.7	3.3
	7.5	6.0	7.6	5.8	101.3	96.7	2.6	2.4
	10.0	8.0	10.4	7.8	104.0	97.5	2.0	3.3
	12.0	10.0	11.9	10.1	99.2	101.0	3.1	1.9

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