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A polyoxy group branched diazo dye as an alternative material for the fabrication of an electrochemical epinephrine sensor

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In the present study, a novel diazo dye with a polyoxy group (2{2[2(2-methoxyethoxy)ethoxy]ethoxy}-5-[(*E*)-(4-nitrophenyl)diazenyl]benzaldehyde (AZOTEG)) was used as a modifier to fabricate modified electrochemical platforms for epinephrine detection. For this purpose, a carbon paste electrode (CPE), which was the working electrode, was modified with AZOTEG molecules. An increase in epinephrine oxidation peak current with a negative shift in peak potentials demonstrated the electrocatalytic effect of the AZOTEG/CPE compared to the plain CPE. After the observation of this effect, experimental parameters like AZOTEG amount and pH were optimized. Then, the electrochemical mechanism was investigated by obtaining cyclic voltammograms *versus* scan rates. Under the optimized conditions, the analytical characteristics were examined and as a result, a wide linear range (0.1–75 μM) with a limit of detection and a limit of quantification of 0.013 μM and 0.042 μM (n = 3) were obtained. After the examination of the interference effect of uric acid, the developed sensor was successfully used for epinephrine detection in adrenaline injection samples.

1. Introduction

Epinephrine, a catecholamine neurotransmitter secreted from the adrenal gland, has crucial roles in the regulation of the central nervous system and glycogen metabolism. Since it is secreted from the adrenal medulla, it is also known as adrenaline and exists in biological fluids as an organic cation. Besides, epinephrine is also used as an emergency health care medication. Its concentration in biological fluids is an indication to diagnose several diseases including Parkinson's disease, thyroid hormone deficiency, diabetes and cerebral malaises. Therefore, its sensitive and accurate quantification plays a key role in terms of pharmacological studies and clinical research studies.[1–5]

Epinephrine is an electroactive molecule which can easily oxidize. This feature can be utilised for epinephrine detection in biological fluids and pharmaceutical formulations by monitoring its oxidation signals *via* electrochemical methods.[6,7] Even though electrochemical methods offer low cost, sensitive and practical detection of epinephrine, there are crucial problems to be solved. Co-existence of several biomolecules (*e.g.* uric acid, dopamine and ascorbic acid) in biological matrices is the most challenging problem which causes the observation of additional oxidation peaks at closer potentials to the epinephrine oxidation potential. The other critical problem is the passivation of the electrode surface due to the polymerization of epinephrine leading to coating of the electrode surface.[6–10] In order to overcome these problems and achieve higher sensitivity, many attempts have been made based on the surface modification techniques so far. Negatively charged or electron-rich molecules have been used for electrode modification with this purpose.[5,8,10–14] Besides, a novel technique comprising centrifugation and voltammetric scanning in the same electrochemical cell was also presented to obtain improved sensitivity for epinephrine detection.[9] Nevertheless, there is an increasing demand for alternative materials to fabricate effective electrochemical platforms for sensitive and practical epinephrine detection.

Apart from its conventional usage as dyes and pigments, diazo compounds were also employed in organic semiconductor devices such as thin film transistors and light emitting diodes. In addition, diazo dyes were utilized in photoresponsive and supramolecular systems as well.[15,16] In sensing and bio-sensing applications, diazo dyes have been chiefly used in the fabrication of optical sensors and chemosensors[17–20] and there are limited papers about their usage in electrochemical sensors and biosensors in the literature.[21–28] Diazo dyes were reported to be used in the dispersion of graphene nanoplatelets in aqueous medium as well as a cross-linker and doping agent in the electropolymerization process among these studies.[21,23] In the majority of the electrochemical studies in the literature, diazo dyes were electropolymerized for the fabrication of modified electrodes and applied to electrochemical

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determination of several molecules such as fenitrothion, 4-nitrophenol and oxadiargyl.[24–26] Diazo dye polymers in combination with nanomaterials were also utilized to develop non-enzymatic glucose and cholesterol biosensors.[27,28] In the present study, a polyoxy group attached diazo dye was directly constructed as a thin film without electropolymerization for the fabrication of modified electrochemical platforms as a new approach. Electrochemical performance of the developed sensor was examined towards epinephrine oxidation and experimental parameters like modifier amount and pH were optimized. Analytical characteristics of the proposed sensor were investigated under optimized conditions and epinephrine amount in adrenaline injection samples was determined.

2. Experimental

2.1. Instrumentation

Voltammetric measurements were performed by using an Autolab PGSTAT 12 potentiostat/galvanostat (Metrohm EcoChimie B.V., Netherlands) controlled by NOVA 1.10 software. A plain or modified carbon paste electrode (CPE), Ag/AgCl (3 M KCl) and platinum wire were utilized as the working, reference and counter electrodes, respectively.

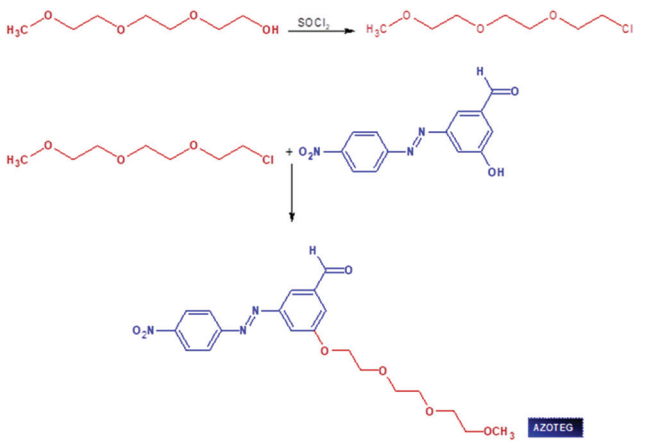
2.2. Reagents and chemicals

All reagents and chemicals used in the experiments were of analytical grade. Fine powdered graphite (Merck) and mineral oil (Sigma-Aldrich) were used for plain and modified electrode fabrication. Dichloromethane (CH_2Cl_2) and methanol (CH_3OH) were purchased from Merck to prepare diazo dye solution. Citric acid monohydrate, trisodium citrate dihydrate, trizma base (Sigma-Aldrich), trizma hydrochloride, and uric acid (Sigma) were procured to perform pH and interference effect studies. Epinephrine stock solution was prepared daily from (±)-epinephrine hydrochloride (Sigma). Phosphate buffer (PB, pH 7.0) containing appropriate amounts of 0.067 M potassium dihydrogen phosphate, KH_2PO_4 (Merck) and 0.067 M sodium monohydrogen phosphate, Na_2HPO_4 (Sigma-Aldrich) was used as a supporting electrolyte. Double distilled water were used in the preparation of solutions.

2.3. Synthesis of 2{2[2(2-methoxyethoxy)ethoxy]ethoxy}-5-[(*E*)-(4-nitrophenyl)diazenyl]benzaldehyde (AZOTEG)

Synthesis of AZOTEG was carried out in three steps as shown in Scheme 1. Each step of synthesis was explained below as also previously described in the literature.[15,16]

2.3.1. Synthesis of 1-chloro-2-[2-(2-methoxyethoxy)ethoxy]-ethane. This was synthesized by following the literature.[16] Briefly, a mixture of triethylene glycol monomethyl ether (0.52 mol), toluene (250 mL) and pyridine (45.3 mL) was heated. At reflux temperature, thionyl chloride (0.52 mol) was added dropwise from a dropping funnel under continuous stirring for 3 h. The mixture was refluxed for an additional 16 h and then allowed to cool down. 20 mL of 0.3 M HCl was added to the mixture at room temperature in a period of 15 min. Consequently, the upper organic layer was removed. The product was obtained as a light yellow oil. Yield: 70%. ^{1}H NMR ($CDCl_3$; d, ppm): 3.55–3.51 (t, 2H, $-CH_2-Cl$), 3.48–3.40 (m, 8H, $-CH_2OCH_2CH_2OCH_2-$), 3.34–3.31 (t, 2H, $-CH_2OCH_3$), 3.16 (s, 3H, $-O-CH_3$); $C_7H_{15}O_3Cl$.



Scheme 1 Synthesis of 2{2[2(2-methoxyethoxy)ethoxy]ethoxy}-5-[(*E*)-(4-nitrophenyl)diazenyl]benzaldehyde (AZOTEG).

2.3.2. Synthesis of 1-(3-formyl-4-hydroxyphenylazo)-4-nitrobenzene. This was synthesized by following the literature.[15]

2.3.3. Synthesis of AZOTEG. AZOTEG was synthesized as described in the literature.[16] 1-Chloro-2-[2-(2-methoxyethoxy)ethoxy]-ethane (2.8 mmol) was added to a mixture of 1-(3-formyl-4-hydroxyphenylazo)-4-nitrobenzene (6.4 mmol) and K_2CO_3 (12.8 mmol) in 20 mL of dimethylformamide under an argon atmosphere. The mixture was heated at 140 °C for 19 h under continuous stirring and finally refluxed for 2 h. The resulting solution was concentrated. The crude product was purified by column chromatography (Silica, $CHCl_3$: MeOH, 10 : 0.5). Yield: 85%. ^{1}H NMR ($CDCl_3$, d 7.26 ppm): 10.05 (1H, s); 8.39 (2H, d); 8.27 (1H, t); 8.22 (1H, t); 8.01 (2H, d); 7.14 (1H, d); 4.3 (2H, t), 3.9 (t, 2H), 3.7 (t, 2H), 3.6 (m, 4H), 3.5 (t, 2H), 3.33 (s, 3H) ppm. $C_{20}H_{23}N_3O_7$.

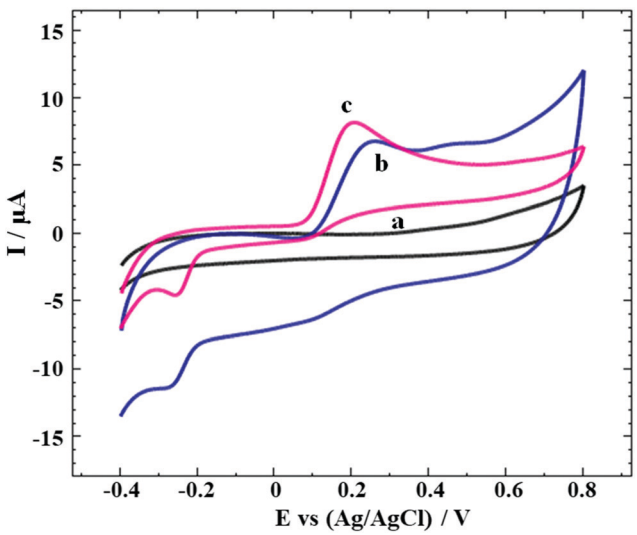


Fig. 1 Cyclic voltammograms recorded for (a) supporting electrolyte (0.067 M PB, pH 7.0), (b) 50 µM epinephrine at the plain CPE, and (c) 50 µM epinephrine at the AZOTEG/CPE at a scan rate of 50 mV s^{-1} with a step potential of 0.00244 V and interval time of 0.048800 s (AZOTEG amount: 10 µL).

2.4. Fabrication of AZOTEG/CPE and the electrochemical procedure

Since CPE was used as a support and also a plain electrode as well, a homogeneous mixture of graphite and mineral oil in 70 : 30 mass ratio was prepared at first. The obtained carbon paste was placed in the electrode cavity and the electrode surface was smoothened on weighing paper. In order to modify the CPE surface, 1 mg of AZOTEG was dissolved in 1 mL of CH_2Cl_2–CH_3OH mixture (1 : 1 by volume). 10 μL of AZOTEG solution was spread onto the CPE surface and left at room temperature for 1 h for the evaporation of the solvent mixture.

The epinephrine stock solution was diluted to the required concentration with supporting electrolyte in a 10 mL electrochemical cell and dissolved oxygen was deaerated *via* nitrogen flow during a period of 3 min. Cyclic and differential pulse voltammograms were recorded by scanning the potential between −0.4 and +0.8 V.

2.5. Sample preparation

Adrenaline injection samples containing 1 mg mL^{-1} epinephrine were diluted 10-fold with 0.067 M PB (pH 7.0) prior to the voltammetric measurement.

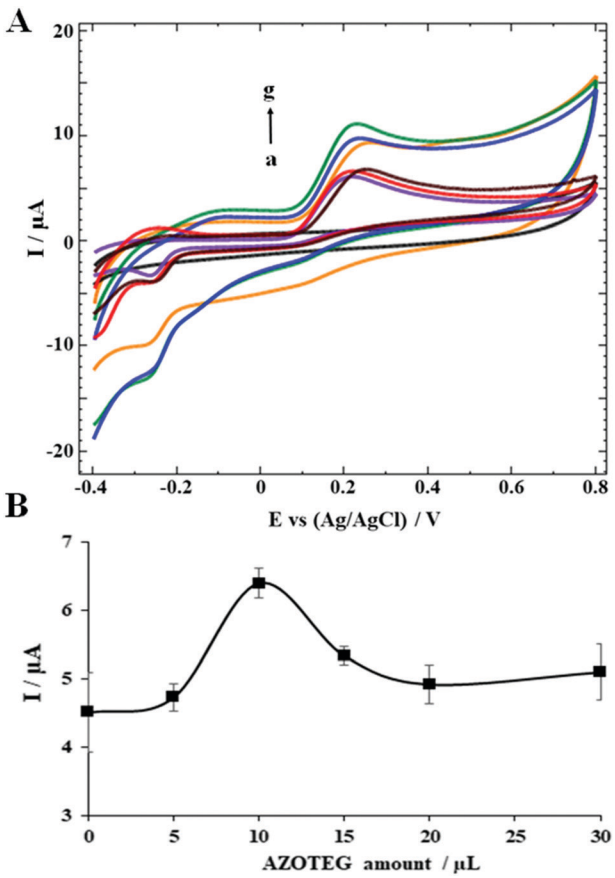


Fig. 2 (A) Cyclic voltammograms of (a) supporting electrolyte (0.067 M PB, pH 7.0) and 50 μM epinephrine obtained at the AZOTEG/CPE modified with different amounts of AZOTEG (b–g: 0, 5, 20, 30, 15, 10 μL) at a scan rate of 50 mV s^{-1} with a step potential of 0.00244 V and an interval time of 0.048800 s. (B) Plot of the epinephrine peak current–AZOTEG amount relationship.

3. Results and discussion

3.1. Electrochemical performances of the plain CPE and AZOTEG/CPE towards epinephrine oxidation

The electrochemical performance of the AZOTEG/CPE was investigated by recording cyclic voltammograms in the presence of 50 μM epinephrine (0.067 M PB, pH 7.0) and compared with the plain CPE (Fig. 1). As demonstrated in Fig. 1, an oxidation peak was observed for the CPE with an anodic peak current

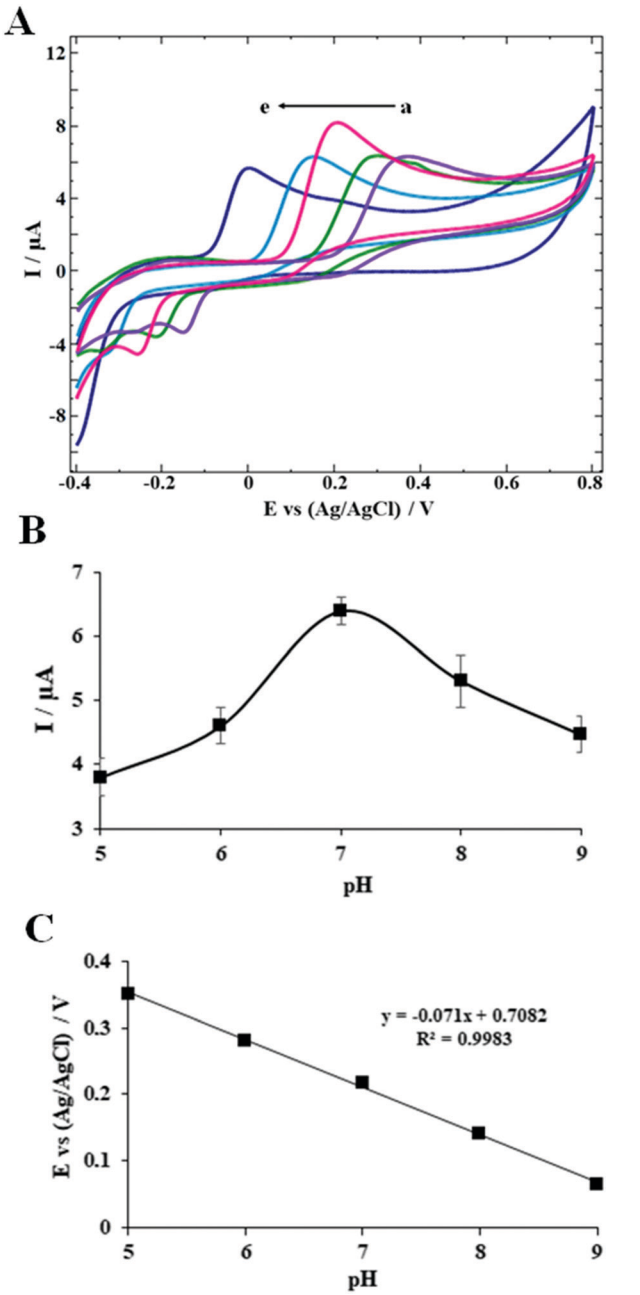


Fig. 3 (A) Cyclic voltammograms of 50 μM epinephrine at different pH values (a–e: 5.0, 6.0, 7.0, 8.0, 9.0) at a scan rate of 50 mV s^{-1} with a step potential of 0.00244 V and an interval time of 0.048800 s, (B) plot of the epinephrine peak current–pH and (C) plot of epinephrine peak potential–pH relationship (AZOTEG amount: 10 μL).

of 4.510 μA at 0.237 V. In the case of AZOTEG/CPE, an epinephrine oxidation peak was obtained at 0.198 V with a peak current of 6.334 μA. Under the same conditions, a 1.4-fold increase in the peak current with a cathodic shift of 39 mV confirmed the electrocatalytic effect of the AZOTEG/CPE towards epinephrine oxidation. Since epinephrine (pK_a = 8.8) is in cationic form at neutral and physiological pH, it may be predicted that positively charged epinephrine may have been attracted by an electron-rich polyoxy group of AZOTEG. Besides, hydroxyl groups in epinephrine are capable of forming hydrogen bonds with oxygen atoms in the AZOTEG structure. Therefore, the facilitated epinephrine oxidation with increased peak current may be attributed to the interaction between AZOTEG and epinephrine.[8,11,29]

3.2. Optimization of experimental parameters

3.2.1. Effect of AZOTEG amount. Modifier amount on the electrode surface is a crucial parameter for the fabrication of an efficient electrochemical sensor since thickness of the modifier layer directly affects the conductivity of the system.[6,10,30] Therefore, AZOTEG amount was changed in the range of 0–30 μL and voltammetric responses of 50 μM epinephrine (0.067 M PB, pH 7.0) were measured at a scan rate of 50 mV s^{-1} (Fig. 2). As can be seen from the figure, the epinephrine oxidation peak current increases up to 10 μL by increasing the amounts of AZOTEG on the CPE surface, whereas larger amounts of AZOTEG lead to a decrease in peak current values.

Thus, 10 μL was selected as the optimum amount of AZOTEG for the modification and used for further experiments.

3.2.2. Effect of pH. Working medium pH is another important parameter to estimate the electrochemical reaction mechanism. In general, electrochemical oxidation or reduction of many organic molecules includes protons. Thus, pH remarkably affects the peak currents and peak potentials of organic molecules in electrochemical reactions.[8,14] Within this purpose, the effect of pH on epinephrine oxidation at the AZOTEG/CPE was investigated between pH 5.0–9.0. It is clearly seen in Fig. 3A and B that the peak current values increases with increasing pH and reaches a maximum at pH 7.0 confirming that protons catalyse the epinephrine oxidation reaction at the AZOTEG/CPE surface. Furthermore, it may also be inferred that the interaction between epinephrine and the polyoxy group of AZOTEG was predominantly maintained at pH 7.0.

On the other hand, a cathodic shift in the peak potentials was observed with increasing pH indicating that protons are involved in the electrochemical oxidation reaction at the AZOTEG/CPE (Fig. 3A). In Fig. 3C, the relationship between pH and peak potentials was found to be linear with a slope value of −0.071 V per pH closer to the theoretical slope value of 0.059 V per pH in the Nernst equation. The obtained data demonstrated that equal numbers of protons and electrons are involved in the electrochemical oxidation reaction of epinephrine at the AZOTEG/CPE surface, which is in accordance with previously reported studies.[1,8,10,11,14]

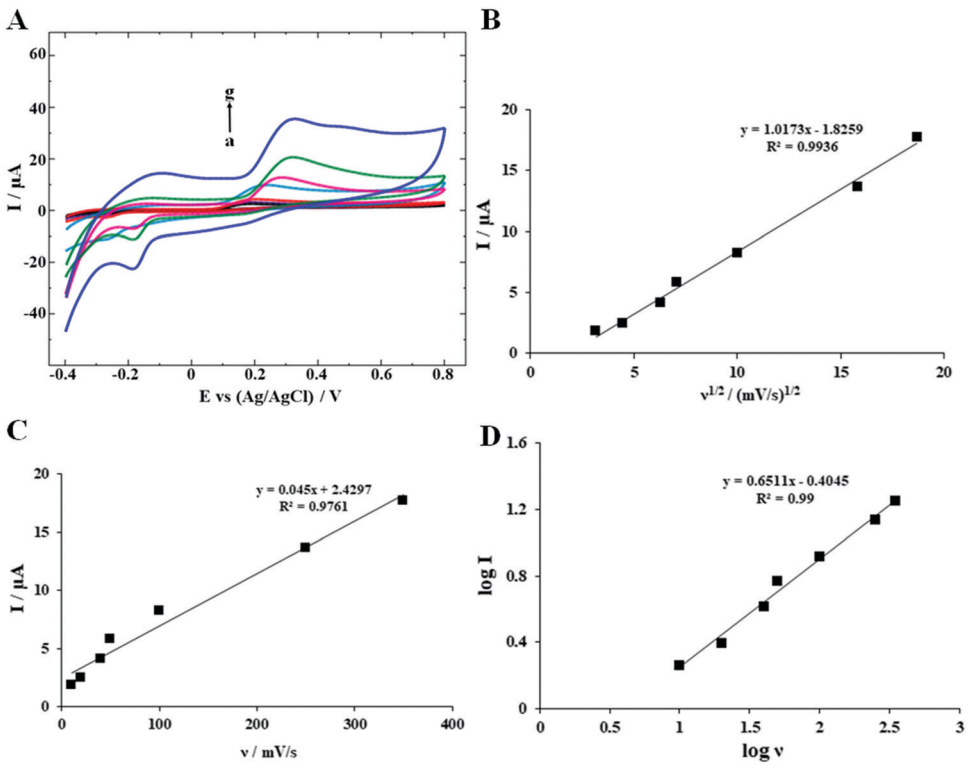


Fig. 4 (A) Cyclic voltammograms of 50 μM epinephrine (0.067 M PB, pH 7.0) at different scan rates (a–g: 10, 20, 40, 50, 100, 250, 350 mV s^{-1}) with a step potential of 0.00244 V and an interval time of 0.048800, (B) plot of epinephrine peak current–square root of scan rate, (C) plot of epinephrine peak current–scan rate relationship, and (D) log *I* *vs.* log ν plot (AZOTEG amount: 10 μL).

3.2.3. Effect of scan rate. Effect of scan rate on epinephrine oxidation was examined by varying the scan rate between 10–350 mV s^{-1} to gain further knowledge about the reaction mechanism on the AZOTEG/CPE. In Fig. 4A, cyclic voltammograms of 50 μM epinephrine (0.067 M PB, pH 7.0) at different scan rates are shown. As can be clearly seen from Fig. 4A, while the epinephrine oxidation peak current values gradually increases, an anodic shift is observed in the peak potentials. Moreover, the relationship between peak current and scan rate was investigated and it was observed that the peak current values linearly increased with the square root of scan rate suggesting a diffusion-controlled process between 10–350 mV s^{-1} (Fig. 4B and C). In order to estimate the prevailing process on the electrode surface, logarithm of peak current ($\log I$) *versus* logarithm of scan rate ($\log \nu$) plot was depicted with a slope value of 0.6511 (Fig. 4D). In theory, a slope value of 0.5 indicates a diffusion-controlled process, whereas a slope value of 1.0 addresses an adsorption-controlled process. The obtained slope value indicates that diffusion is more predominant than adsorption in the reaction mechanism at the AZOTEG/CPE.[31–34]

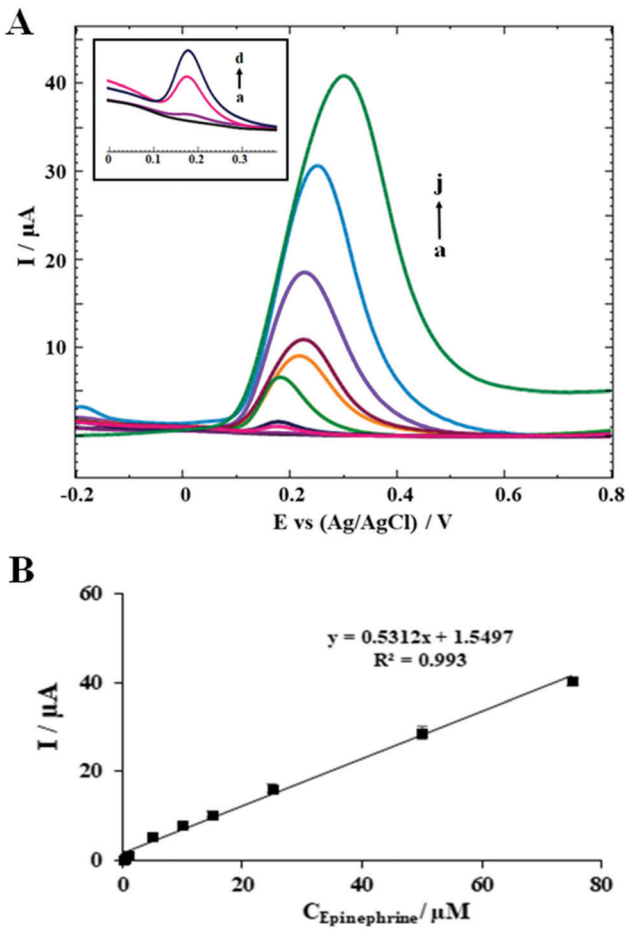


Fig. 5 (A) Differential pulse voltammograms for various concentrations of epinephrine (a: background, b–j: 0.1, 0.5, 1, 5, 10, 15, 25, 50, 75 μM). Inset: Differential pulse voltammograms of lower concentrations of epinephrine (a: background, b–d: 0.1, 0.5, 1 μM) in 0.067 M PB, pH 7.0 and (B) calibration plot in the range of 0.1–75 μM (modulation amplitude: 0.025 V, step potential: 0.00500 V, modulation time: 0.05000 s, interval time: 0.5000 s).

3.3. Analytical characteristics

After the optimization of the experimental parameters, analytical characteristics of the AZOTEG/CPE were examined. For this purpose, the epinephrine concentration was changed in the range of 0.1–75 μM (0.067 M PB, pH 7.0) to depict the calibration graph in Fig. 5. Sensitivity of the sensor was evaluated in terms of limit of detection (LOD) and limit of quantification (LOQ) values. LOD and LOQ were calculated based on the equations of $3s/m$ and $10s/m$ (s: standard deviation of blank solution and m: slope of calibration graph) and found as 0.013 μM and 0.042 μM (n = 3), respectively. Relative standard deviation (RSD) was also calculated for 50 μM to estimate the repeatability and found as 4.34% (n = 3). The linear range and LOD obtained for the AZOTEG/CPE were compared with similar studies in the literature (Table 1). As presented in Table 1, a wide linear range with a lower LOD value were obtained for the AZOTEG/CPE compared to similar studies in the literature.

3.4. Voltammetric response of epinephrine at the AZOTEG/CPE in the presence of uric acid

Uric acid is a naturally found biomolecule in biological fluids with epinephrine and it is a major problem for electrochemical epinephrine detection since its oxidation peak potential is close to the epinephrine oxidation peak potential.[37,38] In order to evaluate the selectivity of the AZOTEG/CPE, the voltammetric responses of 10 μM epinephrine (0.067 M PB, pH 7.0) were examined in the presence of 20 μM and 40 μM uric acid (Fig. 6). A uric acid oxidation peak was not obtained separately at the AZOTEG/CPE and peak shouldering around 0.4 V was attributed

Table 1 Comparison of the fabricated sensor with similar studies for electrochemical epinephrine detection

Electrode	Linear range (μM)	LOD (μM)	Ref.
$NiFe_2O_4$–MWCNTs–GCE[a]	0.1–1000	0.09	1
GCE–MWCNT/Fe_3O_4/29*H*,31*H*-Pc[b]	7.5–48	4.6	3
GCE/Chit-fCNT[c]	0.05–10	0.003	4
EDDPT/GO/CPE[d]	1.5–600	0.65	5
P(L-Asp)/ERGO/GCE[e]	0.1–110	0.025	10
ZnO–GO/SPE[f]	0.5–500	0.07	35
CPE/NiO/CNTs[g]	0.08–900	0.01	36
AZOTEG/CPE	0.1–75	0.013	Present study

[a] $NiFe_2O_4$–MWCNTs–GCE: nickel ferrite magnetic nanoparticles decorated multiwall carbon nanotubes modified glassy carbon electrode. [b] GCE-MWCNT/Fe_3O_4/29*H*,31*H*-Pc: multiwall carbon nanotube/iron oxide nanoparticles/29*H*,31*H*-phthalocyanine hybrid modified glassy carbon electrode. [c] GCE/Chit-fCNT: functionalized multiwall carbon nanotube-chitosan biopolymer nanocomposite modified glassy carbon electrode. [d] EDDPT/GO/CPE: 2-(5-ethyl-2,4-dihydroxyphenyl)-5,7-dimethyl-4*H*-pyrido[2,3-*d*][1,3]thiazine-4-one/graphene oxide modified carbon paste electrode. [e] P(L-Asp)/ERGO/GCE: poly(L-aspartic acid)/electrochemically reduced graphene oxide modified glassy carbon electrode. [f] ZnO–GO/SPE: zinc oxide nanorod–graphene oxide nanocomposite modified graphite screen printed electrode. [g] CPE/NiO/CNTs: nickel oxide/carbon nanotubes nanocomposite modified carbon paste electrode.

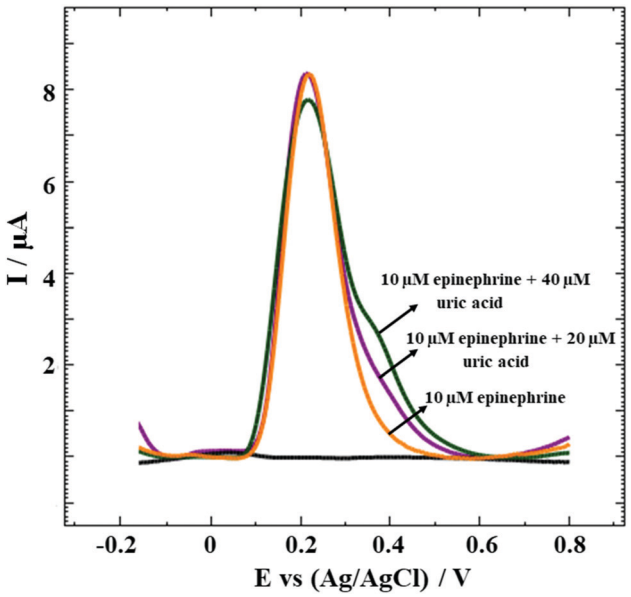


Fig. 6 Differential pulse voltammograms recorded for 10 μM epinephrine, 10 μM epinephrine + 20 μM uric acid and 10 μM epinephrine + 40 μM uric acid (0.067 M PB, pH 7.0) under optimum conditions.

to uric acid oxidation.[37] In spite of shouldering peaks of uric acid, it was observed that the peak currents of 10 μM epinephrine were changed as −1.25% and −4.87% in the presence of 20 μM and 40 μM uric acid, respectively. In addition, the epinephrine oxidation potentials were not shifted due to the presence of uric acid indicating that the voltammetric responses of epinephrine were not significantly affected.

3.5. Epinephrine detection in adrenaline injection samples

The applicability of the developed sensor was evaluated by detecting the epinephrine amount in adrenaline injection samples under the optimized conditions. The recovery value was calculated as 98.7 ± 2.4% (n = 3). It was indicated that the AZOTEG/CPE exhibited satisfactory results for epinephrine detection in real samples.

4. Conclusion

In this study, a polyoxy group containing diazo dye modified electrochemical sensor was fabricated for practical and sensitive epinephrine detection. It was observed that the electrochemical response of epinephrine at the AZOTEG/CPE was improved as attributed to the interaction between epinephrine and polyoxy groups in the AZOTEG structure. Under the optimized conditions, the AZOTEG/CPE exhibited enhanced sensitivity with a wide linear range compared to previously reported studies in the literature. The utility of the AZOTEG/CPE in practical applications was tested for epinephrine detection in adrenaline injection samples. The obtained results showed that diazo dyes with various functional groups may be alternatively used in sensor and biosensor fabrication to determine biologically important molecules unlike their conventional usage.

Conflicts of interest

The authors declare that they have no conflict of interest.

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