

An Electrochemical Sensor Based on Functionalized Carbon Nanotube with Pyrazole Derivative for Determination of Hydrazine

Mohammad Mazloum-Ardakani^{*1}, Zahra Alizadeh¹, Laleh Hosseinzadeh²,
BiBiFatemeh Mirjalili¹, Naeimeh Salehi¹

1. Department of Chemistry, Faculty of Science, Yazd University, Yazd, 89195-741, I.R. Iran

2. Department of Chemistry, Dehloran Branch, Islamic Azad University, Dehloran, Ilam, Iran

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Abstract

In this work, we synthesis and application of functionalized carbon nanotubes (CNTs) with 6-amino-4-(3,4-dihydroxyphenyl)-3-methyl-1,4-dihydropyran[2,3-c]pyrazole-5 carbonitrile (pyrazole derivative (APC)) as sensing platform toward hydrazine (HZ). Electrochemical properties of functionalized carbon nanotubes composite (APC-CNT) were investigated by cyclic voltammetry, chronoamperometry and differential pulse voltammetry techniques. It was found that the APC-CNT composite exhibited a pair of redox peaks, which is due to the electron transfer between the APC and the glassy carbon electrode. The electrocatalytic properties of the APC-CNT composite for HZ oxidation was remarkably increased as compared to only CNTs. The kinetic parameters of the APC-CNT composite in the presence and absence of HZ was studied by electrochemical methods. The APC-CNT modified electrode revealed an excellent voltammetric response to oxidation of HZ with a wide linear range from 0.01 μM to 120.0 μM and limit of detection of 8.6 nM. Also, APC-CNT modified electrode shows high selectivity, good stability, reproducibility with a RSD less than 2.11%.

Keywords

Pyrazole Derivative; Sensor; Carbon Nanotubes; Hydrazine; Modified Electrode.

یک حسگر الکتروشیمیایی مبتنی بر نانوله‌های کربنی عامل‌دار شده با مشتق پیرازول برای تعیین هیدرازین

محمد مظلوم اردکانی^{*۱}، زهرا علیزاده^۱، لاله حسین زاده^۲، بی بی فاطمه میرجلیلی^۱، نعیمه صالحی^۱

۱. بخش شیمی، دانشکده علوم، دانشگاه یزد، دانشگاه یزد، یزد، ایران

۲. بخش شیمی، دانشگاه آزاد اسلامی واحد دهلران، ایلام، ایران

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چکیده

در این تحقیق، نانوله‌های کربنی عامل‌دار شده با ۶-آمینو-۴-(۳-متیل-۱،۴-دی‌هیدروکسی‌فنیل)-۳-متیل-۱،۴-دی‌هیدروپیرانو [۲،۳-سی]پیرازول-۵-کربونیتیل (مشتق پیرازول (APC)) سنتز و بعنوان حسگر هیدرازین بکار برده شد. خواص الکتروشیمیایی کامپوزیت APC-CNT با تکنیک‌های ولتامتری چرخه‌ای، کروئوامپرومتری و ولتامتری پالس تفاضلی مورد بررسی قرار گرفت. کامپوزیت APC-CNT یک جفت پیک اکسایش و کاهش، که به دلیل انتقال الکترون بین APC و الکتروود کربن شیشه‌ای نشان می‌دهد. خواص الکتروکاتالیزوری کامپوزیت APC-CNT برای اکسایش هیدرازین به طور قابل توجهی نسبت به CNT تنها افزایش یافته است. پارامترهای سینتیکی کامپوزیت APC-CNT در حضور و عدم حضور هیدرازین با استفاده از روش‌های الکتروشیمیایی مطالعه شده است. الکتروود اصلاح شده APC-CNT پاسخ ولتامتری بسیار خوبی را برای اکسایش هیدرازین با گستره خطی ۰/۰۱ میکرومولار تا ۱۲۰/۰ میکرومولار و حد تشخیص ۸/۶ نانومولار نشان می‌دهد. همچنین الکتروود APC-CNT انتخاب پذیری بالا، پایداری خوب و تکرارپذیری با RSD کمتر از ۲/۱۱٪ را نشان می‌دهد.

واژه‌های کلیدی

مشتق پیرازول؛ حسگر؛ نانوله‌های کربنی؛ هیدرازین؛ الکتروود اصلاح‌شده.

1. INTRODUCTION

The development of sensitive sensor for hydrazine determination is important since HZ and its derivatives has significant applications as

a blowing agent, corrosion inhibitors, plant growth regulators, photographic, pharmaceutical industries and fuel [1-3]. However, hydrazine is also known to be highly toxic and harmful for

*Corresponding Author: mazloum@yazd.ac.ir

human, especially in high concentrations, leading to varying degrees of damages in central nervous system, vision, spleen, respiratory, liver and kidney [2,4]. Therefore, from industrial and environmental viewpoint, the development of practical methods to detect hydrazine concentration has been in high important. Some analytical methods like HPLC [5], spectrophotometry [6], GC [7], flow detection [8], atomic absorption spectroscopy [9], and electrochemical sensors [10,11] have been proposed for the determination of hydrazine in different types of samples. However, most of these techniques usually are expensive and complicated. Also, these techniques require time-consuming pretreatment steps and trained operators. Among these methods, electrochemical methods have great attention because electrochemical equipment is usually sensitive, simple in detection, compact, and economical in comparison to the traditional equipment [12–15]. Due to the high overpotential and low electron transfer rate of hydrazine, the working electrode should be modified by a modifier to promote a better electron transfer between the hydrazine and electrode. A variety of material such as polymer [16], metal oxides nanoparticles [17], metal sulfides [18], metal nanoparticle [19], and carbon based nanomaterials [20–22] have been used for modification of electrode to improve the electrochemical performance of sensor. Among of carbon based nanomaterials, carbon nanotubes having extensive potential applications as electrocatalysts in electrochemical sensors due to their excellent electronic and catalytic properties. Different strategies have been used to improve the electrochemical performance of carbon nanotubes [23,24]. Recent papers showed that some composite based on carbon nanotubes such as carbon nanotube-wired ZnO nanoflower [11], Ag NP on multi-walled carbon nanotube [25], hematoxylin multi-wall carbon nanotubes [26], fullerene-functionalized carbon nanotubes [27] Core-shell $\text{Fe}_3\text{O}_4@/\text{SiO}_2/\text{MWCNT}$ nanocomposite [28], ellagic acid phytochemical on MWCNT [29] and palladium NPs on multi-walled carbon nanotubes [30] could also act as platform in electrochemical sensors. These composites based on carbon nanotubes could work as efficient sensing platform for hydrazine oxidation reactions. Previously, we have successfully introduced catechol derivative onto carbon nanotubes and used for the electrochemical detection of isoproterenol and serotonin [31]. These composite provide a good electrochemical sensing platform for analytes, and is expected to have widely potential applications in catalysts and

biosensors. The obtained results revealed that direct electron transfer between catechol derivative and the electrode surface can be easily performed at the modified electrode and the nanocomposite system had dramatically enhanced electrocatalytic activity towards analytes [31]. In this direct, our research group modified carbon nanotubes with fullerene for sensor development [32,33]. Here in continuation to our research's regarding the preparation of electrochemical sensors [13–15,34], we developed a pyrazole derivative functionalized carbon nanotubes composite as a new electrocatalyst for the determination of hydrazine in real samples. The combination of pyrazole derivative and carbon nanotubes improved the sensitivity and stability of the proposed sensing platform. This electrochemical sensor showed very efficient electrochemical performance toward electrochemical oxidation of hydrazine.

2. EXPERIMENTAL

2.1. Chemicals and Apparatus

H_2SO_4 , HNO_3 , KCl, hydrazine, ethyl acetoacetate, and ethanol were purchased from Merck (Darmstadt, Germany). The MWCNTs (Outer diameter: 5–20 nm; Innerdiameter: 2–6 nm; length: 1–10 μm and 95% pure) were purchased from Plasma Chem (Germany). Deionized water was used for the fresh preparation of all solutions. Morphologies of the CNTs were characterized using a scanning electron microscopy (SEM, Hitachi S-4160). Electrochemical measurements were accomplished on a potentiostat/galvanostat (SAMA 500, Iran). All experiments were performed by a three-electrode system with a platinum wire and an Ag/AgCl/KCl were employed as a counter and reference electrodes, respectively. The glassy carbon electrode (GCE, 3mm diameter, Azar electrode) applied as a working electrode.

2.2. synthesis of 6-Amino-4-(3,4-dihydroxyphenyl)-3-methyl-1,4-dihydropyranol[2,3-c]pyrazole-5-carbonitrile

In a mortar, a mixture of ethyl acetoacetate (1 mmol) and hydrazine derivatives (1.5 mmol) was ground with a pestle at room temperature for 1 min. Then, 3,4-dihydroxy benzaldehyde (1 mmol), malononitrile (1 mmol) and nano- $\text{SiO}_2/\text{DABCO}$ (0.05 g) were added to the reaction mixture and was ground continuously at room temperature. After completion of reaction (as indicated by TLC, ethyl acetate: n-hexane, 20:80), the reaction mixture was dissolved in EtOH. Then, the catalyst was filtered off and the obtained solution was poured into cold water, filtered and dried at room temperature

2.3. Characteristics of 6-Amino-4-(3,4-dihydroxyphenyl)-3-methyl-1,4-dihydropyrano [2,3-c] pyrazole-5-carbonitrile:

White solid, m.p. 225-227°C. FT-IR (ATR) $\bar{\nu}$ (cm⁻¹): 3458, 3247, 3129, 2180, 1627, 1595, 1514, 1491, 1397, 1265, 1183, 1106, 1049, 754. ¹H NMR (250 MHz, DMSO-d₆) δ ppm: 12.02 (s, NH, 1H), 8.82 (s, OH, 1H), 8.70 (s, OH, 1H), 6.75 (s, NH, 2H), 6.61 (dd, J=7.5 Hz, J=1.5 Hz, 1H), 6.42-6.45 (m, 2H), 4.35 (s, 1H), 1.78 (s, 3H).

2.4. Preparation of the pyrazole derivative functionalized carbon nanotubes composite

The functionalized carbon nanotubes composite were prepared by treating CNTs with a mixture of concentrated H₂SO₄ and HNO₃ following the method reported in the literature [35]. In a typical experiment, 36.0 mL of H₂SO₄ and 12.0 mL of HNO₃ were mixed and added to 100 mg of CNTs in a an ultrasound bath for 2 h to give a suspension. It was allowed to cool down to room temperature in overnight. The suspension was centrifuged and the then washed several times with deionized water and drying at 60 °C for 24 h. The APC-CNT composite was prepared by mixing 4.0 mg of APC and 1.0 mg of CNTs in 4 mL of deionized water under stirring for 24 h at room temperature. The suspensions were centrifuged, and the samples were thoroughly rinsed with water to removal of the free APC from CNT and then dried.

2.5. Preparation of the electrode

For preparation of the modified GCE with prepared composite, the bare GCE was polished with alumina powder and then cleaned alternately in distilled water. After that, a suspension was prepared by dispersing a 1 mg of APC-CNT composite in 1 mL deionized water. Finally, 2.5 μ L of APC-CNT composite suspension was dropped onto the clean GCE surface and drying at room temperature.

3. RESULT AND DISCUSSION

3.1. Electrochemical properties of APC-CNT composite

Fig. 1 shows CVs of APC-CNT/GCE in phosphate buffer solution (pH 8.0). A pair of well-defined CV peaks observed for APC-CNT/GCE with anodic and cathodic peak potentials, E_{pa}, E_{pc}, of 60 and 10 mV, respectively. The peak separation potential, (ΔE_p) of 50 mV, is higher than the 59/n mV expected for a reversible redox system, suggesting that the APC in APC-CNT has a quasi-reversible behavior in aqueous medium. The effect of the potential scan rate on redox system of the APC-CNT/GCE was also investigated by CV. Plots of both I_{pa} and

I_{pc} were linearly dependent on scan rate in the range of 20–3000 mVs⁻¹ (Fig. 2), indicating that the redox properties of APC at the composite film on electrode is diffusion less in nature. Also, the peak separation (ΔE_p) has increased with the scan rate. The peak current in buffer solutions is related to the surface coverage of APC, therefore, surface coverage of the APC on the composite film can estimated by Sharp method [36]. From the slope of I_{pa} versus scan rate (inset a in Fig. 2) the calculated surface concentration of APC is 2.63 $\times 10^{-10}$ mol cm⁻².

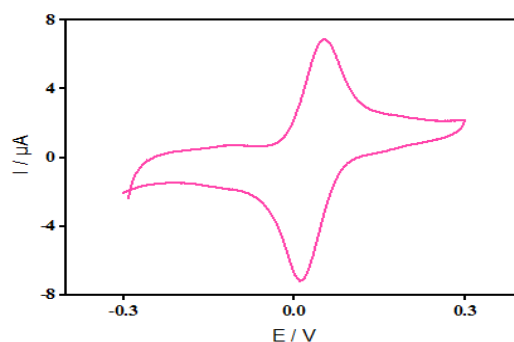


Fig. 1. CV of APC-CNT/GCE in 0.1 M phosphate buffer solution (pH 8.0) at scan rate of 20 mVs⁻¹.

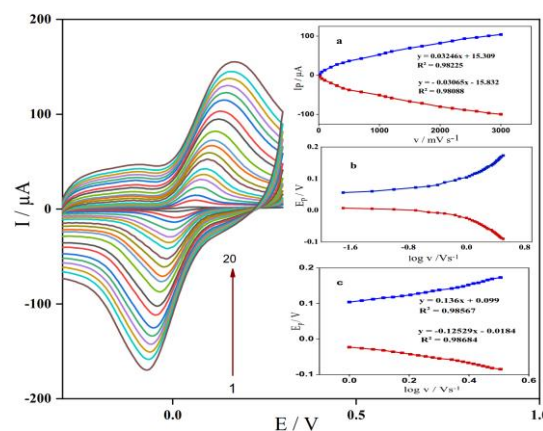


Fig. 2. CVs of APC-CNT/GCE in 0.1 M Phosphate buffer (pH 8.0) at different scan rates, from down to up: 20-50-100-200-300-400-500-700-800-1000-1100-1200-1500-1700-2000-2200-2400-2600-2800-3000, insets: (a) variation of Ip vs. scan rate; (b) and (c) Ep vs. the logarithm of scan rates.

The electron-transfer rate constant, k_s , can be obtained from variation of anodic and cathodic peak potentials (E_p) with the logarithm of the scan rate (inset b in Fig. 2), according to Laviron method [37]. The slopes of these plot can be used to calculate the cathodic and anodic transfer coefficients. The evaluated value for the α_a and α_c is 0.54 and 0.46, respectively. By cathodic and anodic transfer coefficients, we could calculate k_s for APC-CNT modified electrode. The value of k_s = 5.7 s⁻¹ was evaluated by Laviron method [37].

The oxidation peak of the APC-CNT/GCE is pH dependent. Thus, the CV behavior of the APC-CNT/GCE was investigated at different pHs (pHs= 3.0–11.0). E_{pc} and E_{pa} of the APC-CNT/GCE were moved toward less potentials with increases in pH. Inset Fig. 3 shows E_p -pH diagram, indicating that the E_p values as a function of pH. This diagram is consist of a straight line with slope = 57.2 mV/pH. This slop suggests the Nernst equation for a two electron and proton transfer reaction.

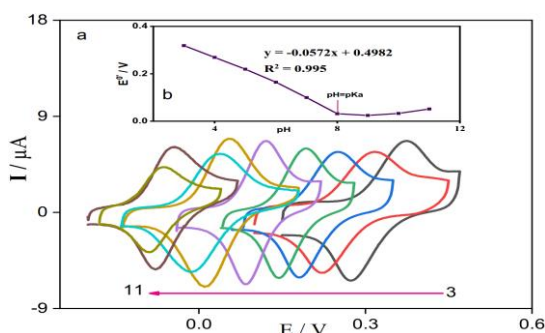
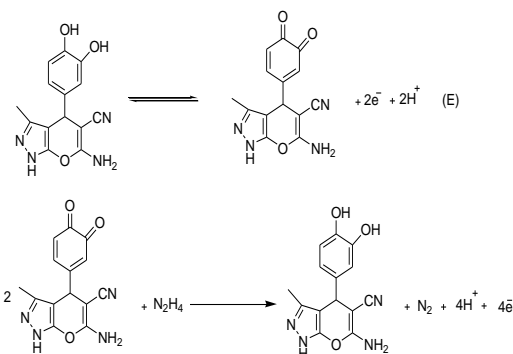


Fig. 3. CVs of APC-CNT/GCE in 0.1 M phosphate buffer solution (pH 8.0). pH values from (3) to (11) Scan rate: 50 mV s^{-1} . Inset: Variation of E_p as a function of pH.

3.2. Electrocatalytic properties of the APC-CNT composite electrode for hydrazine

The cyclic voltammetry characteristic of the GCE and APC-CNT composite on glassy carbon electrode (APC-CNT/GCE) were evulated in buffer solution (pH 8.0) in the absence and presence of 0.6 mM hydrazine at the scan rate of 25 mVs^{-1} demonstrated in Fig. 4. As can be seen, in the absence of hydrazine, no detectable signal is obtained on GCE (curve a); but, in the presence of hydrazine a weak CV signal is observed (curve b) at the same scan rate of potential, at about 0.4 V that showed in Fig.4. On the other hand, the corresponding potential at APC-CNT/GCE is 0.08 V (curve f). Based on these results peak potential for hydrazine oxidation at the APC-CNT/GCE move by about 0.32 V to less potential compared to GCE. However, APC-CNT/GCE (curve f) shows higher current toward hydrazine compared to APC/GCE (curve e), indicating that the presence of APC on the CNTs could enhance the peak currents, which may due to the excellent electronic and catalytic properties of CNTs such as good electrical conductivity, high chemical stability and high surface area. The APC-CNT/GCE in 0.1 M phosphate buffer solution (pH 8.0), in the absence of hydrazine shows a redox reaction (curve d) after addition of 0.6 mM hydrazine; the I_{pa} of the modified electrode by APC-CNT composite

was considerably increased (3.95 times), while the cathodic peak related to APC disappeared (curve e). Based on these observations, an electrocatalytic behavior is proposed for hydrazine reaction at the modified electrode by APC-CNT composite via an EC' catalytic mechanism (Scheme 1). In this mechanism, hydrazine is oxidized in the catalytic chemical reaction (in 80 mV) by the APC_{ox} and produced in electrochemical reaction (E). The effect of potential scan rate (v) on electrochemical properties of modified electrode by APC-CNT composite has been evaluated in the range of 5–30 mV/s (Fig. 5). The I_p slightly moved to high potential with increase in scan rate. However, I_p enhanced with the increase of scan rate (inset a at Fig. 5) and showed a linear behavior to the square root of the scan rate, which indicates a surface-controlled electrochemical reaction [38]. The Tafel plot obtaeind from inset Fig. 5B, which indicates that a one-electron transfer process is a rate-limiting step assuming a transfer coefficient (α) is about 0.51.



Scheme 1. Electrocatalytic reactions mechanism for hydrazine at surface of APC-CNT/GCE

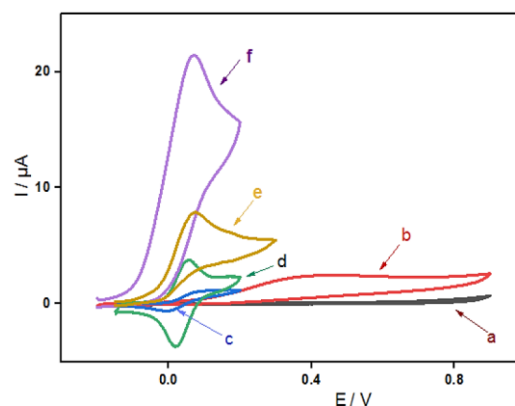


Fig. 4. CVs of (a) unmodified GCE in 0.1 M phosphate buffer solution (pH 7.0) at scan rate of 25 mV s^{-1} ; (b) as (a) + 0.6 mM hydrazine; (c) as (a) at the surface of APC- GCE; (d) as (a) at the surface of APC-CNT/GCE; (e) as (c) + 0.6 mM hydrazine; (f) as (b) at the surface of APC-CNT/GCE.

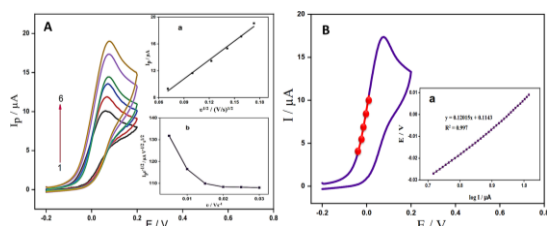


Fig. 5. (A) Cyclic voltammograms of APC-CNT/GCE in 0.1 M phosphate buffer solution (pH 8.0) in percent of 0.6 mM hydrazine at different scan rates, from down to up: 5, 10, 15, 25 and 30 mV s^{-1} ; variation of (a) anodic peak current vs. $v^{1/2}$ and (b) Variations in scan rate normalized current ($I_p / v^{1/2}$) with scan rate, (B) Tafel plot derived from the rising part of voltammogram recorded at a scan rate of 20 mV s^{-1} .

3.3. Chronoamperometric measurements

Chronoamperometric investigation of hydrazine at APC-CNT/GCE was done for different concentrations of hydrazine (Fig. 6), with a diffusion coefficient of D , and the Cottrell equation describes the mass transport limited current for the electrochemical reaction [38]. It was observed that the plot of I vs. $t^{-1/2}$ is linear for various concentrations of hydrazine, according to the slope and Cottrell equation the mean value of the D was found to be $2.41 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ (Fig. 6). Chronoamperometry can also be employed to investigate the catalytic rate constant, k_h , for the reaction between hydrazine and the APC-CNT composite [39]. According to the method of Galus, the average value of k_h was found to be $1.99 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$.

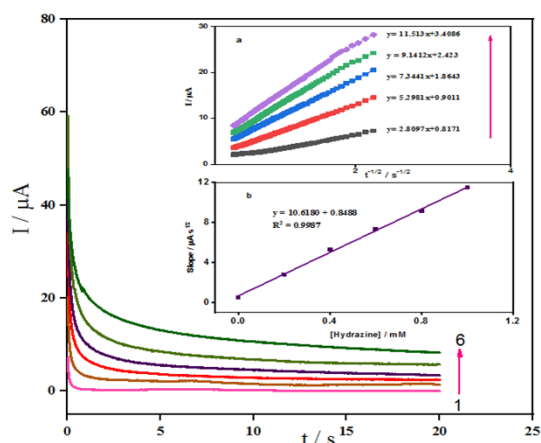


Fig. 6. Chronoamperograms obtained at APC-CNT/GCE in 0.1 M phosphate buffer solution (pH 8.0) for different concentrations of hydrazine. The numbers 1–5 correspond to 0, 0.2, 0.4, 0.6, 0.8 and 1.0 mM of hydrazine. Insets: (A) plots of I vs. $t^{-1/2}$ obtained from chronoamperograms, (B) plot of the slope of the straight lines against the hydrazine concentration.

3.4. Calibration plot and limit of detection

Fig. 7 shows typical differential pulse voltammetry (DPV) curves of hydrazine in

phosphate buffer solution (pH 8.0) at the APC-CNT/GCE with successive addition of hydrazine. The anodic current increased with the addition of hydrazine. The regression equation for hydrazine in the range of 0.01–2 μM was $I_p (\mu\text{A}) = (10.83) C_{\text{hydrazine}} + (6.42)$ ($R^2 = 0.996$), while the regression equation for hydrazine in the range of 2–120 μM was $I_p (\mu\text{A}) = (0.221) C_{\text{hydrazine}} + (42.1)$ ($R^2 = 0.990$). Therefore, as it can be seen in inset A of Fig. 7, the oxidation of current linearly with the concentration of hydrazine in the range of 0.01 μM to 120 μM , and a detection limit of 8.6 nM. The present modified electrode by APC-CNT composite displayed an excellent performance with a good wide linear range and high sensitivity.

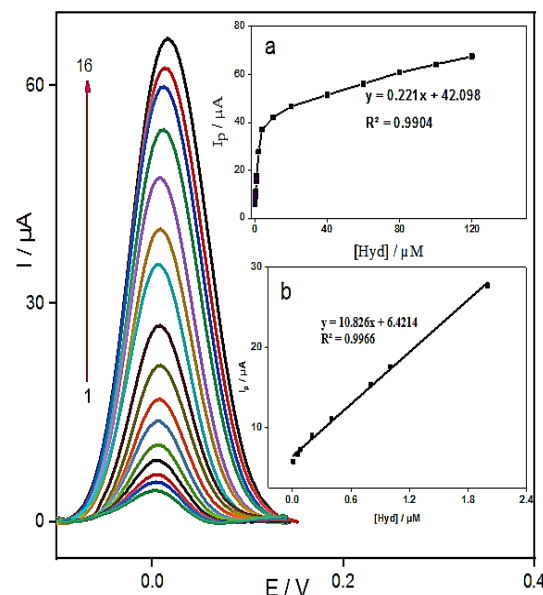


Fig. 7. Differential pulse voltammograms of APC-CNT/GCE in 0.1 M PBS (pH 8.0) containing different concentrations of hydrazine. The numbers 1–16 correspond to: 0.01, 0.05, 0.08, 0.2, 0.4, 0.8, 1.0, 2.0, 4.0, 10, 20, 40, 60, 80, 100 and 120 μM of hydrazine. Inset plots of electrocatalytic peak current as a function of hydrazine concentration.

3.5. Real samples measurement

To explore the performance of the proposed modified electrode based on APC-CNT composite in real sample analysis, the hydrazine concentration drinking water samples is determined. The samples examined were found to be free from hydrazine. For preparation of synthetic samples known amounts of hydrazine added to drinking water samples. The results of real sample investigation are listed in table 1, according to the presented results the modified electrode based on APC-CNT composite is applicable and acceptable for determination of hydrazine in real samples.

Table 1. The application of APC-CNT/GCE for determination of hydrazine in water samples.

Hydrazin Added (μM)	Found (μM)	(%) Recovery	(%) RSD
0	-	-	-
20.0	20.5	102.5	3.2
40.0	40.6	101.5	1.6
60.0	59.4	99.0	2.8

3.6. The repeatability and stability of APC-CNT/GCE

To evaluate generate a reproducible surface of APC-CNT/GCE was examined using cyclic voltammetry from five separately prepared APC-CNT/GCE. The RSD for DPV determination of 50 μM hydrazine was 2.11%, indicated that surface reproducibility was acceptable. In addition, the repeatability of proposed modified electrode was investigated by DPV of 50 μM hydrazine. The relative standard deviation (RSD%) for ten successive measurements was 1.59%. This study shows APC-CNT/GCE has a good reproducibility and repeatability for electrochemical determination of hydrazine.

4. CONCLUSION

In brief, a novel composite based on pyrazole derivative (APC) on the CNTs modified GCE was prepared for electrocatalytic determination hydrazine. The CV and DPV studies showed effective electrocatalytic activity of the APC-CNT/GCE in decreasing the anodic overpotential for the oxidation of hydrazine. This APC-CNT composite modified electrode shows perfect sensing properties including high sensitivity, low detection limit and fast response time. These properties may impute to the CNTs provides a large surface area for APC. Furthermore, the test results of determination in real samples showed that the APC-CNT/GCE is acceptable for determination of hydrazine in drinking water samples.

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