



Original scientific paper

Novel electrochemical sensing platform for detection of hydrazine based on modified screen-printed graphite electrode

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Abstract

The current work aimed to fabricate a screen-printed graphite electrode (SPGE) modified by MnO₂ nanorods (MnO₂ NRs) for sensing hydrazine. Thus, a facile protocol was adopted to construct the MnO₂ nanorods that were subsequently applied to modify the SPGE surface directly. As-synthesized MnO₂ NRs/SPGE sensor exhibited a strong sensing behavior towards the hydrazine, with a large peak current and small oxidation potential. This electrochemical sensor in the optimized conditions to detect the hydrazine possessed a low detection limit (0.02 μM), a broad linear dynamic range (0.05-275.0 μM) and an admirable sensitivity (0.0625 μA μM⁻¹). The sensor applicability was practically estimated in real water samples, which revealed successful recovery values.

Keywords

MnO₂ nanorods; electrochemical sensor; hydrazine diffusion coefficient

Introduction

Hydrazine, a vital chemical reagent, has attracted widespread research interest due to its industrial application and poisonousness. It is a robust reducing agent with various applications in the production of pesticides and medicine [1-3]. It is also a chemical deoxidizer with broad applications as an oxygen scavenger in water boilers [4]. Hydrazine is a key raw material in the construction of rockets and explosives [5,6]. Although hydrazine plays a great role in human production and life, it is easy to be absorbed by living organisms. The persistent contact with this agent may be associated with complications, such as some disturbances in the reproductive system, central nervous system, liver, kidneys and lungs [7-9]. According to the U.S. Environmental Protection Agency (US EPA), hydrazine is positioned in a class of possibly carcinogenic to humans, with a recommended threshold limit value (TLV) of less than 10 ppb [10].

Accordingly, it is substantial to achieve a practical and efficient sensing protocol for the determination of this agent in various media. In this regard, different analytical and instrumental

protocols have been designed to detect hydrazine so far, such as gas chromatography, capillary electrophoresis, chemiluminescence, high-performance liquid chromatography, liquid chromatography, colorimetry, and spectrophotometry [11-17]. Despite the unique benefits of each of these techniques, they typically require precision instrumentation and length of time. Among these, electrochemical approaches have been concerned by many researchers owing to their peculiar traits, which are simplicity, rapidity, affordability and short response time [18-34]. Voltammetric measurements typically use economical manners to detect analytes by recording variations in response current over alteration in electrode potential [35-42].

The recent development of electrochemical approaches has been greatly simplified by screen-printed electrodes (SPEs) due to their high sensitivity, functionality and versatility [43-45]. The main performance features of a sensor are all gathered in SPEs, including cost-effectiveness, minimal sample preparation, ease of operation, high speed, small size, limited background, and comfortable surface modification. There is always a need for further research to develop electrode materials to improve the selectivity and sensitivity of electrochemical sensors [46-51]. Many advances in nanotechnology have been made in diverse fields in recent years [52-75], which have led to the introduction of highly efficient sensing platforms. Types of nano-scale materials have so far been identified with distinct physicochemical properties that can be employed in the electrochemical sensors to detect various analytes exhibiting admirable results [76-82].

A popular oxide material is manganese dioxide (MnO_2), whose behavior can be enhanced by changing its morphology and surface area. MnO_2 is a polymorph owing to an octahedral [MnO_6] spatial arrangement. Nano-sized MnO_2 exhibits commendable benefits due to a larger surface-to-volume ratio and further reactive surface for electrochemical reactions. The diverse application of this substance in electrochemistry and sensor fabrication can be attributed to the simple reduction of MnO_2 to Mn_2O_3 and MnO and, at the proper potential, the re-oxidation to MnO_2 as a catalytic circle for electrochemical detection [83-87].

The current work aimed to fabricate a new screen-printed graphite electrode (SPGE) supported by MnO_2 nanorods (MnO_2 NRs/SPGE) for sensitively sensing hydrazine. The sensor applicability was tested in real water samples, the results of which revealed successful recovery values.

Experimental

Chemicals and instrumentations

All materials with analytical grades applied throughout this work were supplied from Aldrich and Merck. Electrochemical experiments were recorded using a PGSTAT-302N Autolab potentiostat/galvanostat (Eco Chemie, The Netherlands). The control of all experiments was carried out by a General Purpose Electrochemical System (GPES) software. The SPGEs were purchased from DropSens (Spain) and consisted of an Ag pseudo-reference electrode, graphite auxiliary electrode, and graphite working electrode. All pH values were measured by a digital Metrohm 710 pH meter.

Synthesis of MnO_2 nanorods

The MnO_2 NRs were obtained by dissolving KMnO_4 (0.316 g) in deionized water (30 mL) while vigorously stirring, followed by the addition of 3 M HCl (1.4 mL) under vigorous stirring for another half hour. Then, the solution was placed in a 50-mL Teflon-lined autoclave at 160 °C for six hours. Next, the products were cooled down to room temperature and subsequently centrifuged and thoroughly rinsed with ethanol and deionized water to clean any impurities, followed by drying at 60 °C for 12 h.

Preparation of MnO₂ NRs/SPGE

First, 1 mg of prepared MnO₂ nanorods was added into an aqueous solution (1 ml), followed by sonication for 30 min to give a homogeneous solution. Then, 4 μ L of MnO₂ NRs was dispersed on the surface of SPGE dropwise. Following the solvent's evaporation, the sensor's surface was washed several times with deionized water to clean free modifier molecules and subsequently air-dried. The obtained electrode was noted as MnO₂ NRs/SPGE.

Results and discussion

Characterization of MnO₂ nanorods

Figure 1 illustrates the FE-SEM images captured for the as-fabricated MnO₂ NRs, and observing them confirmed rod-shaped MnO₂ nanorods with a thickness ranging from 15 to 25 nm and a length of about 3 μ m. The MnO₂ NRs showed an almost uniform size distribution.

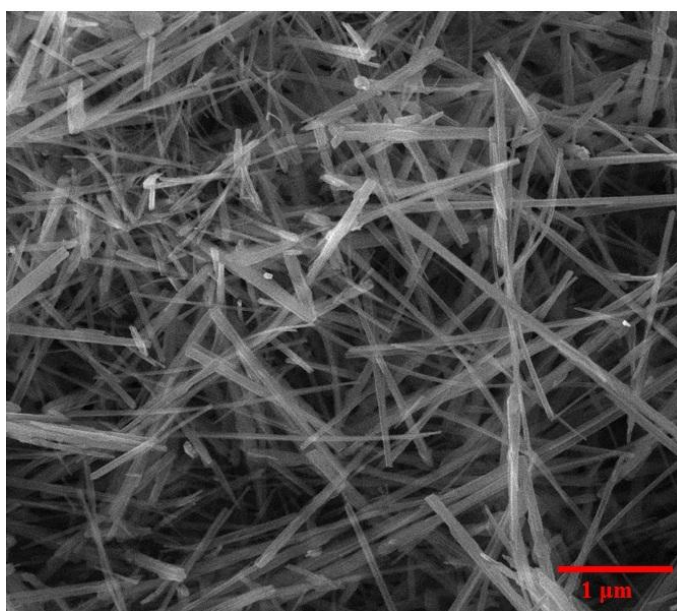


Figure 1. The FESEM image of synthesized MnO₂ nanorods

Electrochemical response of hydrazine at different electrodes

The differential pulse voltammetry (DPV) method was recruited to study the effect pH value of electrolyte solution in different pH values (2.0-9.0) in the presence of 40.0 μ M of hydrazine in phosphate buffer solution (0.1 M PBS) on the MnO₂ NRs/SPGE surface. The peak current of hydrazine oxidation was maximum at the pH value of 7.0, thereby selecting this value as the optimum pH in the hydrazine detection.

Figure 2 shows the application of the cyclic voltammetry (CV) method to evaluate the electrochemical behavior of 200.0 μ M hydrazine at different electrodes (unmodified SPGE, and MnO₂ NRs/SPGE) in PBS (0.1 M, pH 7.0) at the scan rate of 50 mV/s. Based on the results, there was an oxidation peak on the surfaces of the electrodes, but no reduction peak, highlighting an irreversible electrochemical response of hydrazine on the electrodes. A relatively wide and weak peak current (I_{pa}) of hydrazine oxidation was found on the unmodified SPGE (at 1000 mV with 3.0 μ A), which reveals that the electrochemical oxidation does not happen spontaneously due to high activation overpotential. The hydrazine I_{pa} on MnO₂ NRs/SPGE, when compared with unmodified SPGE, displayed further elevation to 13.0 μ A, meaning an increase up to 4.3 times that on the unmodified SPGE. In addition, hydrazine oxidation occurred at a lower potential than unmodified SPGE.

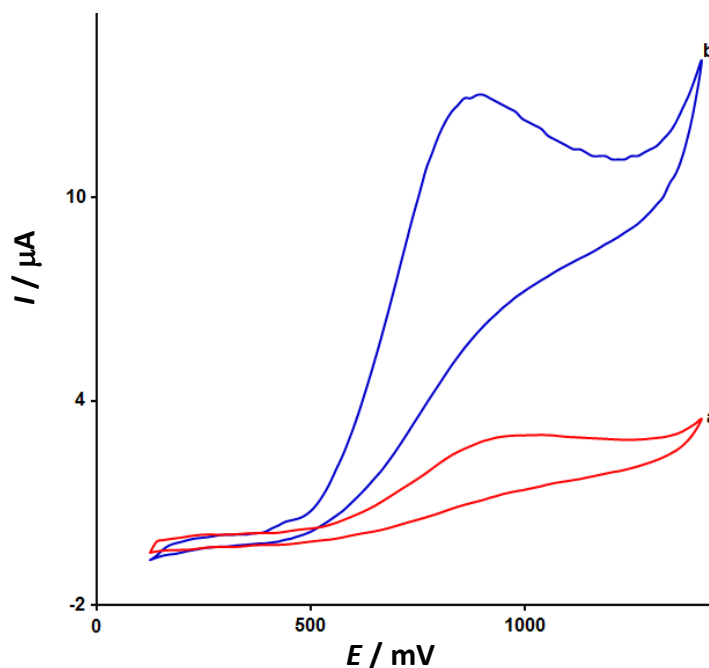


Figure 2. CV curves of unmodified SPGE (curve a), and MnO_2 NRs/SPGE (curve b) in 0.1 M PBS containing 200.0 μM hydrazine; scan rate: 50 mV s^{-1}

Effect of the scan rate (ν) on the results

The influence of various scan rates between 10 and 400 mV/s on the anodic peak currents for hydrazine (100.0 μM) was studied using the MnO_2 NRs/SPGE (Figure 3). The regression equation was $I_{\text{pa}}(\text{hydrazine}) = 1.7036 \nu^{1/2} - 4.2319$ ($R^2=0.9994$) (Figure 3, inset). This result indicates that the oxidation process is controlled by diffusion. Further, there was a shift in the oxidation peak potential of hydrazine toward a more positive potential by increasing the scan rates.

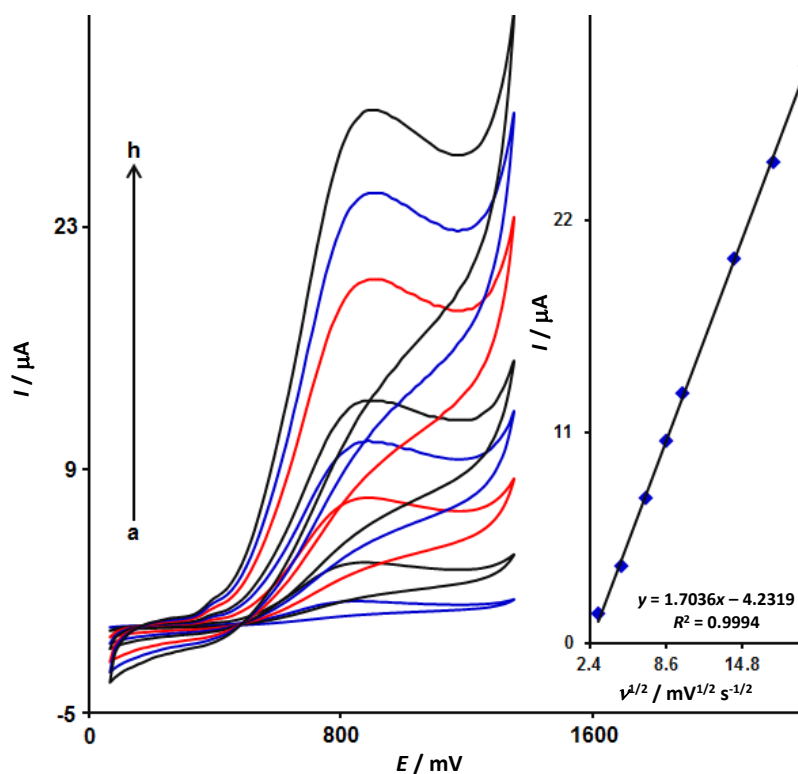


Figure 3. CV curves of 100.0 μM hydrazine in 0.1 M PBS (pH 7.0) at a scan rate of 10 to 400 mV s^{-1} for MnO_2 NRs/SPGE (a-h refer to 10, 25, 50, 75, 100, 200.0, 300.0 and 400.0 mV s^{-1})
Inset: plot of the square root of the scan rate vs. the oxidation peak current of hydrazine

To study the rate-determining step as shown in Figure 4, the data of the rising part of the current-voltage curve obtained at 10 mV/s scan rate were applied to draw a Tafel plot for 100.0 μM of hydrazine. The linearity of the E versus $\log I$ plot, implies the intervention of the kinetics of the electrode process. The slope of this plot was utilized to estimate the number of electrons transferred in the rate-determining step. Figure 4 shows the Tafel slope of 0.2153 V for the linear section of the plot, which means the rate-limiting step of one-electron transfer with a transfer coefficient of $\alpha = 0.72$.

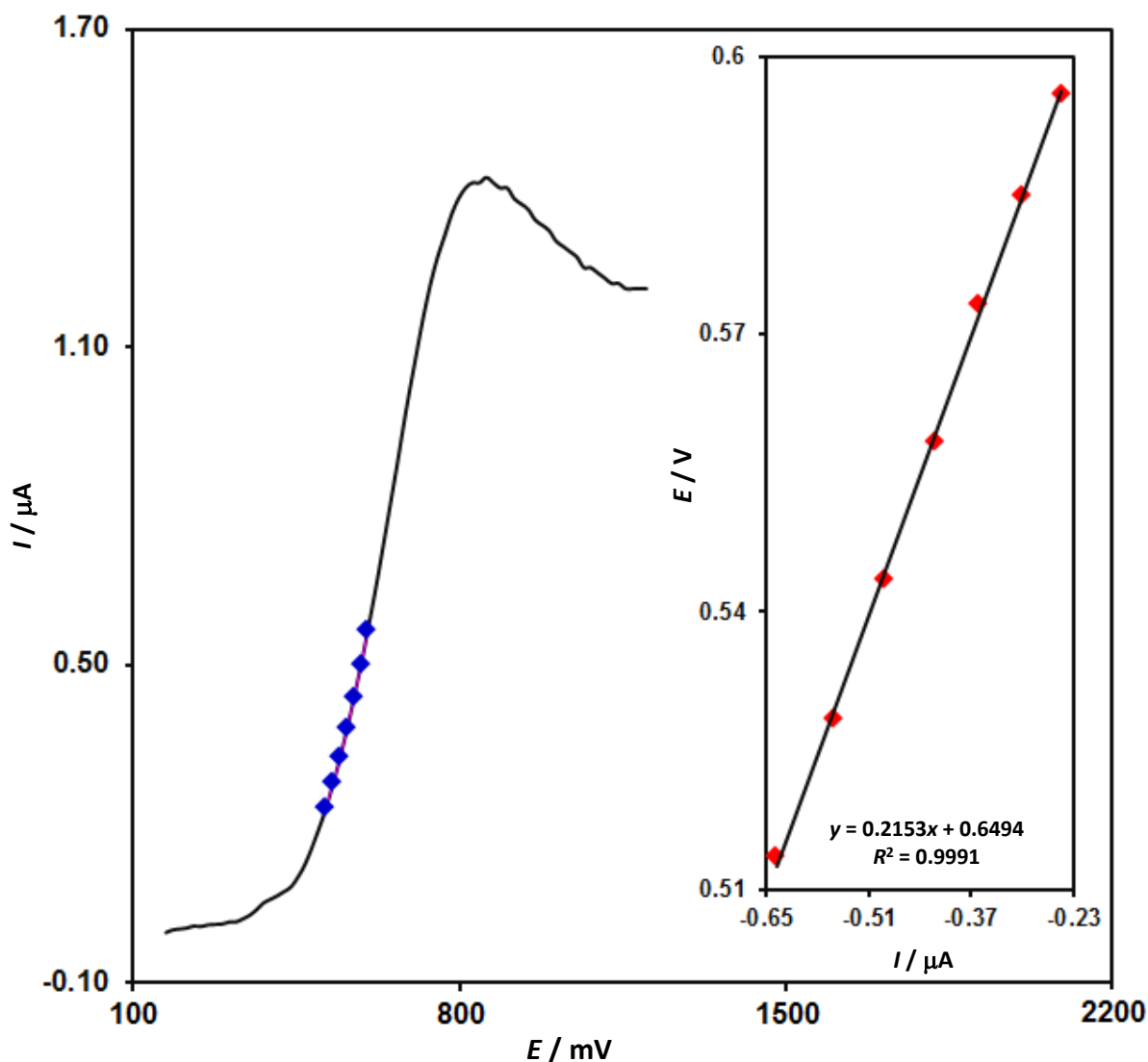


Figure 4. CV response for 100.0 μM hydrazine with 10 mVs^{-1} scan rate and the inset is the Tafel plot derived from the rising part or the corresponding voltammogram

Chronoamperometric analysis

Chronoamperometric determinations for different concentrations of hydrazine on the surface of MnO_2 NRs/SPGE were measured by adjusting the potential of the working electrode at 0.94 V in PBS (0.1 M, pH 7.0), see Figure 5. For an electroactive material (hydrazine in this case) with a diffusion coefficient of D , the current observed for the electrochemical reaction at the mass transport limited condition is described by the Cottrell equation [88]. As shown in Figure 5A, I versus $t^{-1/2}$ plots were used with the optimal fit for various hydrazine concentrations. We drew the slopes from straight lines against different concentrations of hydrazine, see Figure 5B. According to the Cottrell equation and obtained slope, the mean D value was $2.7 \times 10^{-5} \text{ cm}^2/\text{s}$.

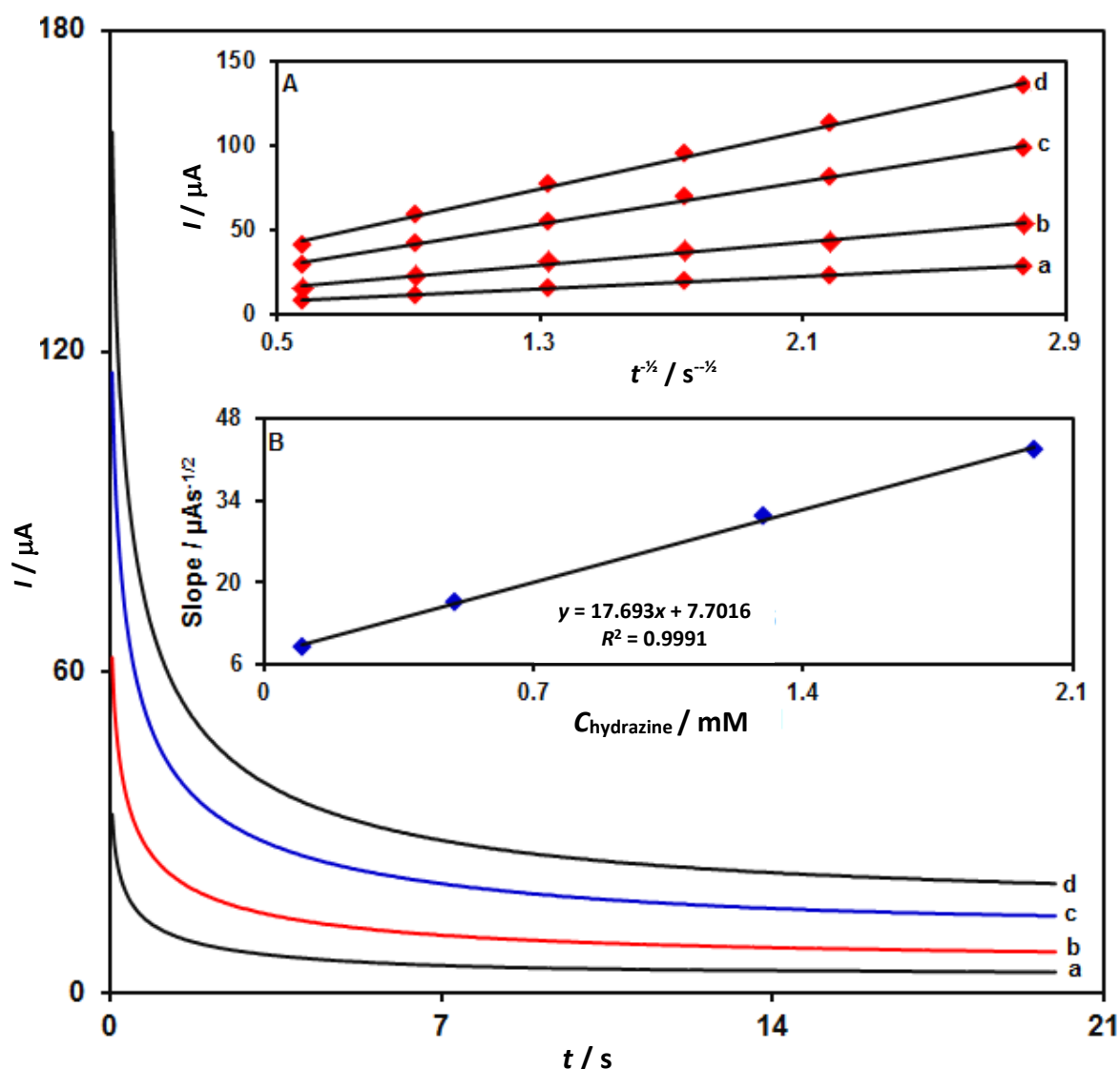


Figure 5. The chronoamperograms obtained at MnO_2 NRs/SPGE in 0.1 M PBS at pH of 7.0 for different concentrations of hydrazine. a-d are related to 0.1, 0.5, 1.3, and 2.0 mM of hydrazine
 Inset A: the I plot versus $t^{-1/2}$ observed by chronoamperograms a to d.
 Inset B: slope plot of the straight line vs. concentration of hydrazine

Calibration curve, linear range and detection limit

MnO_2 NRs/SPGE sensor was used to electrochemically detect different hydrazine concentrations (Figure 6). A gradual elevation was observed for the peak currents of hydrazine oxidation by raising its concentrations, which means an advanced performance of our sensor in the electrocatalytic oxidation of hydrazine. Oxidation peak currents of hydrazine versus $C_{\text{hydrazine}}$ (Figure 6, inset) showed a wide linear range from 0.05 to 275.0 μM . The detection limit ($\text{LOD} = 3\sigma/S$; where σ is the standard deviation of blank response, and S is the slope of the calibration curve with a linear range of concentrations of the analyte) was calculated to be 0.02 μM .

Interference study

The effect of some interference species on the determination of hydrazine was studied. The results show that the interfering effects of glucose, sucrose, urea, uric acid, Na^+ , Cl^- , NO_3^- , pb^{2+} , and Ag^+ on the anodic peak current of hydrazine is less than 5%. Hence, the MnO_2 NRs/SPGE has a superior selectivity for hydrazine.

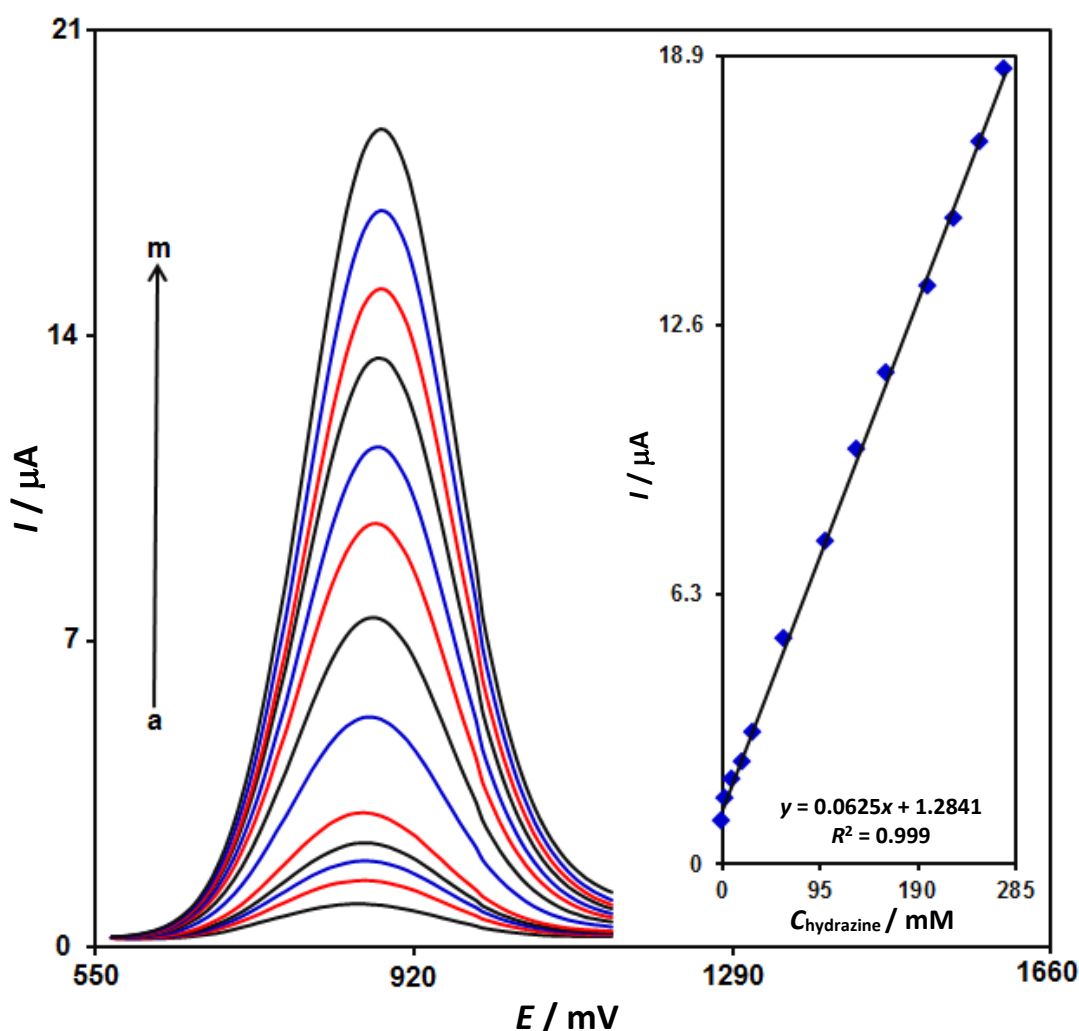


Figure 6. DPV responses of hydrazine on MnO₂ NRs/SPGE at different hydrazine concentrations (a-m refer to: 0.05, 3.0, 10.0, 20.0, 30.0, 60.0, 100.0, 130.0, 160.0, 200.0, 225.0, 250.0 and 275.0 μM) in 0.1 M PBS (pH 7.0). Inset: The relationship between the oxidation peak currents and [hydrazine]

Analytical application

The detection of hydrazine in the water samples (drinking water and tap water) was performed using MnO₂ NRs/SPGE sensor. The concentration values of hydrazine were calculated via the method of standard addition. Attained findings are summarized in Table 1, the recovery is between 96.7 and 102.5 %, and the relative standard deviations are all less than or equal to 3.0%. The experimental results confirmed that the MnO₂ NRs/SPGE sensor has great potential for analytical application.

Table 1. Determining hydrazine in water samples through MnO₂ NRs/SPGE (n=3)

Sample	C / μM		Recovery, %	RSD, %
	Spiked	Found		
Drinking water	0	-	-	-
	4.0	4.1	102.5	3.2
	6.0	5.8	96.7	2.4
Tap water	0	-	-	-
	5.0	4.9	98.0	1.9
	7.0	7.1	101.4	3.0

Conclusion

The present work utilized an ultra-facile protocol to construct MnO₂ nanorods-modified SPGE (MnO₂ NRs/SPGE) for the electrochemical determination of hydrazine. According to CV findings, the as-fabricated sensor exhibited an electrocatalytic performance compared with the unmodified SPGE for the oxidation of hydrazine. The linear current response to the hydrazine level was between 0.05 and 275.0 μM , and the limit of detection was 0.02 μM with a sensitivity of 0.0625 $\mu\text{A } \mu\text{M}^{-1}$. The diffusion coefficient for hydrazine using MnO₂ NRs/SPGE, $2.7 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$, was obtained. The developed sensor applicability was practically tested to detect the concentrations of hydrazine in real water samples, which revealed successful recovery values.

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