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Original scientific paper

Fabrication of a sensitive electrochemical sensor based on CuS-modified carbon paste electrode for hydrazine analysis in water samples

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Abstract

A new electrochemical sensor based on a CuS-modified carbon paste electrode (CPE) was fabricated for the determination of hydrazine. In comparison with the bare CPE, the CuS-modified electrode significantly enhanced the electrooxidation performance of hydrazine by reducing the oxidation overpotential and increasing the oxidation peak current. Differential pulse voltammetry was used as the analytical method for the quantitative determination of hydrazine. The anode peak current was linearly related to hydrazine concentrations between 0.06 and 270.0 µM with a detection limit of as little as 0.02 µM. The sensor modification also showed good stability, reproducibility, and sensitivity. In addition, experimental results demonstrated the reliability and effectiveness of the sensor in determining hydrazine in various types of water samples.

Keywords

Differential pulse voltammetry; CuS nanosheets, environmental pollutants, chemically modified electrode

Introduction

The carbon paste electrode (CPE) was originally reported by Adams in 1958 and is an excellent breakthrough in electrochemical sensor technology [1]. CPEs have generated considerable interest in electrochemical research due to their features, including ultra-low background current, ease of preparation, wide electrochemical window, renewable surface, very low noise levels, low cost, and the convenience of incorporating many modifying agents into the carbon matrix [2]. Although these advantages exist, one of the major drawbacks of CPEs is the low electrical conductivity of the oil-based binders typically used, which hinders electron transfer kinetics and leads to increased peak separation [2]. To address this limitation, various approaches have been investigated, among which

the addition of nanomaterials, such as metal sulphides (MSs), has proved to be viable due to their excellent conductivity [3]. Nanostructured metal sulphides have been of significant concern as a result of their use in a variety of areas, such as electrocatalysis, optoelectronics, chemical and biosensing, biomedicine, and energy. Notably, copper sulphide nanomaterials have proven to be efficient nanocatalysts for various electrochemical reactions [4].

Hydrazine is a strong reducing agent and is widely used in various industries, including rocket fuel propellant, fuel cells, and herbicide production. Derivatives of hydrazine are also used as chemical foam agents or intermediate drugs during the production of drugs [5]. Owing to its superior functional properties and extensive industrial applications, hydrazine toxicity and potential carcinogenicity pose serious health and safety risks [5]. Its strongly toxic and chemical nature can lead to severe health problems such as nausea, dizziness, irritation of the bronchial tract, convulsions, temporary blindness, headache, skin and eye irritation, and possible liver, kidney, and central nervous system damage [6].

In the context of these hazards, selective and precise identification of hydrazine is of crucial concern. Classical analysis methods like titrimetry [7], amperometry [8], potentiometry [9], spectrophotometry [10], and chromatography [11] have been utilized for determining the concentration of hydrazine. Classical approaches are primarily hindered by a series of drawbacks, including lengthy processsing times, high operational costs, specialised equipment and facilities, and skilled personnel [7-11].

Due to these limitations, detection devices that are not only environmentally friendly and sensitive but also economical and selective are becoming increasingly necessary. Electrochemical sensing methods are proving to be a promising alternative with high selectivity and sensitivity, rapid response times, mobility, and ecological acceptability. Over the past few years, electrochemical methods have become increasingly crucial in detecting hydrazine and other toxic substances [12]. Their performance largely relies on the selection of electrode materials, which are crucial in ensuring sensor reliability and performance [13,14].

Chemically modified electrodes (CMEs) are electrodes of conducting or semiconducting substrates coated with a particular chemical modifier film, which can be monomolecular, multimolecular, ionic, or polymeric. To convert its interaction with the target analyte into an electrochemical signal whose amplitude can be measured, the modified surface is equipped with an electrochemical transducer. CMEs' efficiency, requiring very little reagent for analysis, is another advantage. CMEs are also more selective with fewer interference effects [15-18].

In this work, CuS nanosheets were prepared and characterized for precisely this goal. The nanosheets were then further used to modify a carbon paste electrode, which allowed efficient electrocatalytic oxidation as well as sensitive detection of hydrazine. The resulting modified electrode was further successfully used in the quantitative analysis of hydrazine in real sample matrices.

Experimental

Chemicals and apparatus

Electrochemical measurements were made in an Autolab potentiostat/galvanostat system (model PGSTAT 302N, Eco Chemie, The Netherlands), and control of experiments and data acquisition was made through general-purpose electrochemical software. The experimental setup utilized a standard three-electrode arrangement with an Ag/AgCl reference electrode (RE), platinum wire counter electrode (CE), and unmodified carbon paste electrode (CPE) or CuS-modified carbon paste electrode (CuS/CPE) as the working electrode (WE). Chemicals and reagents, such as hydrazine, were analytical-grade and obtained from Merck (Darmstadt, Germany). Buffer solutions

of the pH range 2.0 to 9.0 were prepared from ortho-phosphoric acid and the corresponding phosphate salts.

Synthesis of CuS nanostructures

CuS nanostructures were prepared in a solvothermal reaction, as described by Ke *et al.* [19], but with some modifications in the process. Precisely, 0.225 g (1.3 mmol) copper(II) chloride dihydrate ($CuCl_2 \cdot 2H_2O$) was dissolved in 28 mL of polyethylene glycol-400 (PEG-400) under stirring for 15 min continuously. Afterwards, 0.196 g (2.6 mmol) thioacetamide was added to the solution, followed by 15 minutes of stirring and ultrasonic treatment at 60 °C for 15 minutes. The combined solution was then charged into a Teflon-lined stainless steel autoclave (50 mL volume) and maintained at 180 °C for 15 hours. The resulting solid product was washed several times with ethanol and distilled water, and vacuum-dried overnight at 65 °C.

Electrode preparation

CuS/CPE sensor was prepared by manually mixing 196.0 mg of graphite powder, 4.0 mg of the CuS nanosheets, and a suitable quantity of paraffin oil in a mortar with a pestle until a homogenous paste was achieved. Some of the mixture was filled into the cavity of a glass tube, with a copper wire present at the back end to act as an electrical contact. The paste surface was smoothed and levelled by soft tissue paper, and the electrode surface was polished before application to provide reproducible electrochemical behaviour.

Preparation of samples

The water samples taken from local river and lab were initially filtered through a membrane filter to remove particulates and then diluted in 0.1 M PBS at pH 7.0 for electrochemical analysis. The actual samples were measured in terms of the content of hydrazine using the CuS/CPE sensor prepared and authenticated by the standard addition method.

Results and discussion

Electrochemical behaviour of hydrazine

For the proper quantification of the electrochemical activity of hydrazine, it was necessary to determine the optimal pH, as the redox process is highly sensitive to pH. The experiments were conducted using modified electrodes within a pH range of 2.0 to 9.0. The highest current toward the oxidation of hydrazine was achieved at pH 7.0 and hence this was taken as the optimal pH for further research.

Figure 1 shows linear sweep voltammograms at 200.0 µM hydrazine on an unmodified carbon paste electrode (CPE, curve a) and CuS-modified CPE (CuS/CPE, curve b). The data reflect a significantly higher oxidation signal on CuS/CPE, with the oxidation peak occurring at approximately 900 mV, approximately 100 mV more negative than on the unmodified electrode. Such a shift characterizes the electrocatalytic activity of CuS toward hydrazine oxidation.

Effect of scan rate

The variation in scan rate effect on the hydrazine oxidation current was investigated using linear sweep voltammetry. As shown in Figure 2A, higher anodic peak currents are observed at higher scanning rates, indicating an increased electrochemical response. Plotting I_p against $v^{1/2}$ yielded a linear plot (Figure 2B), indicating that hydrazine oxidation is primarily controlled by diffusion.

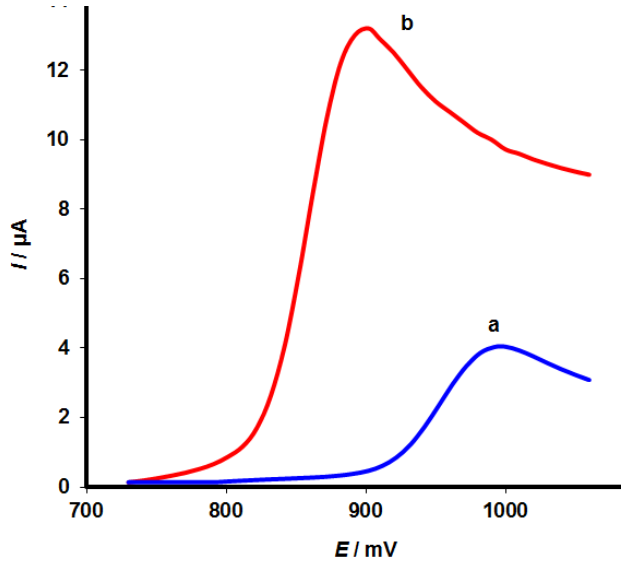

Figure 1. *The linear sweep voltammogram of (a) bare CPE and (b) CuS/CPE in 0.1 M PBS (pH 7.0) in the presence of 200.0 µM hydrazine at the scan rate 50 mV s^{-1}*

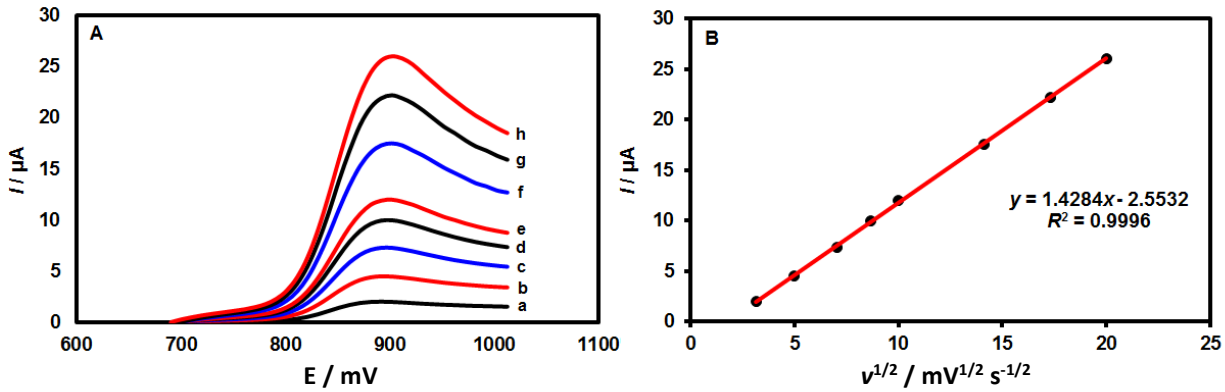

Figure 2. *(A) Linear sweep voltammogram of CuS/CPE in 0.1 M PBS solution (pH 7.0) containing 100.0 µM hydrazine at different scan rates. a-h indicate 10, 25, 50, 75, 100, 200, 300 and 400 mV s^{-1}, (B) anodic peak current height vs.* $v^{1/2}$

Chronoamperometric analysis

Chronoamperometric responses were carried out with the CuS/CPE electrode at a constant potential of 0.95 V. Chronoamperograms for different concentrations of hydrazine in 0.1 M PBS (pH 7.0) are shown in Figure 3A. The result was studied using the Cottrell equation, yielding the diffusion-limiting current response of an electroactive species. Figure 3B plots current (*I*) against the inverse square root of time ($t^{-1/2}$) with a linear profile at varied hydrazine concentrations. Figure 3C is a plot of the slopes of these linear plots against hydrazine concentrations. The diffusion coefficient (*D*) was determined from the slope of the Cottrell equation and computed to be about 2.07×10^{-6} cm² s^{-1}.

Calibration curve

Quantitative analysis of hydrazine was conducted using a CuS-modified carbon paste electrode (CuS/CPE), with anodic peak current responses serving as the analytical signal (Figure 4). Differential pulse voltammetry (DPV) was utilized because it offers better sensitivity and analytical reliability. Based on experiments, it was noted that a distinct linear relationship between oxidation peak current and hydrazine concentration exists within 0.06 to 270.0 µM. The calculated detection limit (LOD) for hydrazine in the given conditions was 0.02 µM.

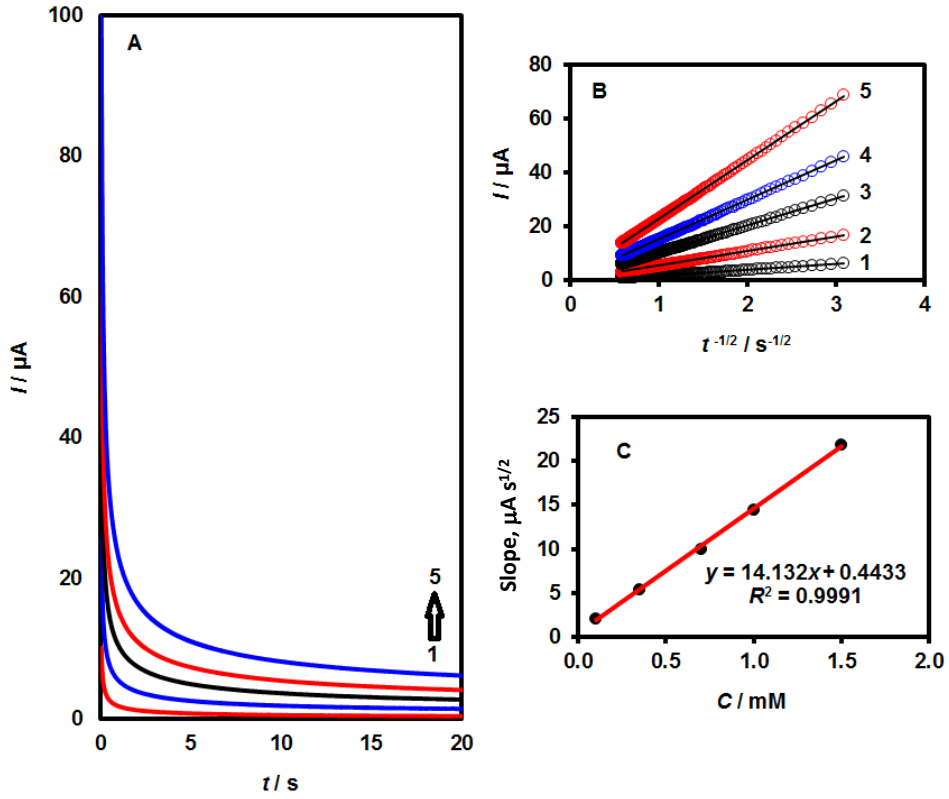

Figure 3. *(A) Chronoamperograms recorded at CuS/CPE in 0.1 M PBS (pH 7.0) for different concentration of hydrazine. Numbering 1 to 5 represent 0.1, 0.35, 0.7, 1.0 and 1.5 mM of hydrazine, (B)* I *plot* vs. $t^{-1/2}$ *recorded from chronoamperograms 1 to 5, (C) Slope plot of straight lines vs. hydrazine concentration*

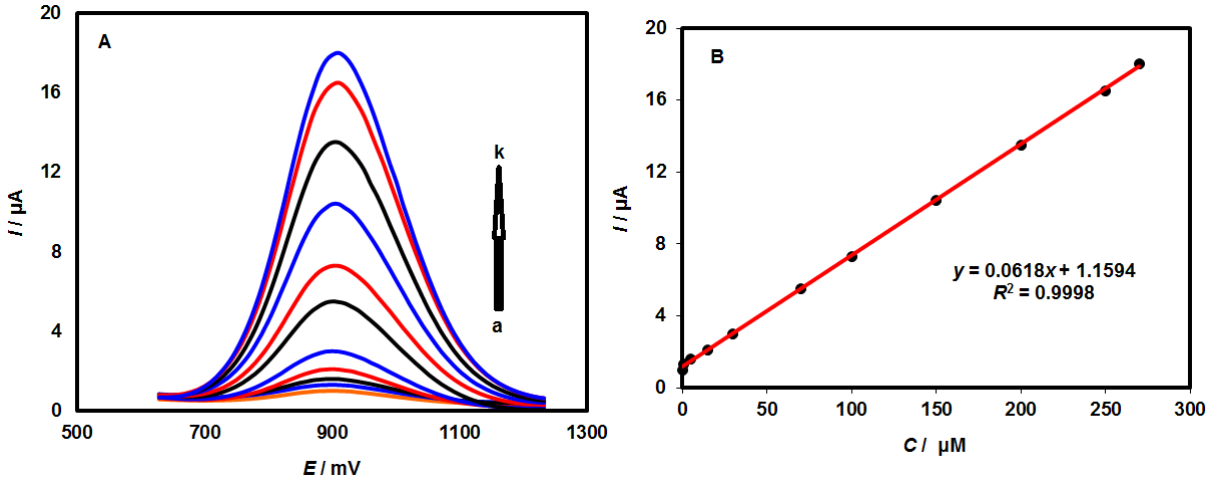

Figure 4. *(A) Differential pulse voltammograms of CuS/CPE in the 0.1 M PBS (pH 7.0) containing diverse hydrazine concentrations. Letters a-k represent 0.06, 1.0, 5.0, 15.0, 30.0, 70.0, 100.0, 150.0, 200.0, 250.0 and 270.0 µM of hydrazine, (B) The plot of peak current vs. hydrazine concentrations between 0.06 and 270.0 µM*

Iterability and stability of CuS /CPE

The stability of the CuS/CPE operation was evaluated by storing the electrode in PBS at a pH of 7.0 for 14 days. Cyclic voltammetry was measured at a 50.0 µM concentration of hydrazine both before and after storage. Results revealed that there was no noticeable change in the oxidation potential of hydrazine but only a very minor loss of ~2.5 % in current response, establishing the high stability of the electrode. To assess antifouling characteristics, the modified electrode was subjected to potential

cycling (15 cycles at 50 mV s^{-1}) in the presence of hydrazine. Minimal current attenuation (~2.7 %) and stable peak positions were observed, suggesting excellent resistance to surface fouling during repeated usage.

Interference examinations

To evaluate the selectivity of the CuS/CPE sensor under optimized conditions, various potentially interfering substances commonly found in pharmaceutical and biological matrices were tested. The tolerance threshold was defined as the maximum concentration of interfering species that caused less than ±5 % deviation in hydrazine measurement. Interference studies showed that substances such as L-lysine, glucose, NADH, acetaminophen, uric acid, various amino acids (*e.g.* L-asparagine, L-serine), carbohydrates (lactose, sucrose, fructose), benzoic acid, alcohols (methanol, ethanol), urea, caffeine, dopamine, neurotransmitters (epinephrine, norepinephrine, serotonin), ascorbic acid, isoproterenol, levodopa, carbidopa, and various metal ions (Mg^{2+}, Al^{3+}, NH_4^+, Fe^{2+}, Fe^{3+}, F^-, SO_4^{2-}, S^{2-}) did not interfere significantly with hydrazine detection, affirming the high selectivity of the sensor.

Analysis of actual samples

To illustrate the usability of the sensor prepared in real-case applications, water samples were examined for hydrazine presence by applying the standard addition technique. The analytical results provided in Table 1 indicate a good recovery of hydrazine and a reasonable relative standard deviation (RSD), thus ensuring the trustworthiness of the method for analysing actual samples.

Table 1. *The application of CuS/ CPE for the determination of hydrazine in real samples (n=5)*

Sample	Spiked concentration µM	Found concentration, µM	Recovery, %	RSD, %
Drinking water	0	-	-	-
	4.0	4.1	102.5	3.4
	8.0	7.9	98.7	2.1
River water	0	-	-	-
	5.0	4.9	98.0	1.8
	10.0	103.0	103.0	3.4

Conclusion

In this paper, CuS nanosheets were successfully obtained and used to fabricate a CuS-modified carbon paste electrode (CuS/CPE). The modified electrode showed enhanced electron transfer capability and superior electrocatalytic performance for hydrazine oxidation under mild experimental conditions. Additionally, the sensor had a wider linear detection range and a significantly lower limit of detection (LOD). The CuS/CPE also demonstrated superior stability, reproducibility, and selectivity. These favourable characteristics facilitated its successful usage for the precise determination of hydrazine in true sample matrices.

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