Electrocatalytic oxidation of hydrazine by copper iodide modified sol-gel derived carbon-ceramic composite Electrode

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CHRONICLE	ABSTRACT
	A new sol-gel derived ceramic-carbon composite electrode was fabricated by the use of CuI as modifier. The electrocatalytic activity of the copper iodide modified sol-gel derived ceramic-carbon composite (CIM-SGD-CCC) electrode was examined for the oxidation of hydrazine. Cyclic voltammetry was employed to study the electrochemical and electrocatalytic properties of the modified electrode. Results showed that the CIM-SGD-CCC electrode has very high catalytic activity for electrooxidation of hydrazine. This proves that the copper iodide bears the main role in electro-catalytic oxidation of hydrazine. This modified electrode shows fast amperometric response with the range from 1 μ mol L^{-1} to 40 μ mol L^{-1} and the limit of detection (LOD) of 0.524 μ mol L^{-1} for hydrazine. The relative standard deviation (R.S.D.) was 0.72 % for 5 successive assays. High stability, good reproducibility, rapid response, easy surface regeneration and fabrication are the important characteristics of the proposed electrode.

1. Introduction

Although metals such as Pt, Au, and Ag are very active in the anodic oxidation and cathodic reduction, they are too expensive for practical applications.[1,2] The use of bare electrodes for electrochemical investigations have a number of limitations, such as low sensitivity and reproducibility, slow electron transfer reaction, low stability over a wide range of solution composition and high overpotential at which the electron transfer process occurs. Many attentions are focused on modified electrodes. Chemically modified electrodes (CMEs) have played an important role in the studies of electrocatalysis[3-5] electron transfer kinetics,[6] membrane barriers[7] and electroorganic synthesis.[8] In operation, the redox active sites shuttle electrons between the analyte and the electrodes with significant reduction in activation overpotential. To prepare the CME, most often a thin film of selected chemical is either bound or coated on to the electrode surface to endow desirable properties of the film in rationally and chemically designed manners.

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The development of chemically modified electrodes (CMEs) made by insoluble inorganic modifiers is motivated by their potential applications and usage in the field of electrocatalysis, electrochromism, solid-state batteries, electrode materials, and electroanalytical applications. These inorganic materials must gain acceptance in practical applications after high chemical and electrochemical stability along with a simple preparation.

However, the main problem is that it is difficult to maintain long-term stability, since the electrochemical activity of modified electrode gradually decreases due to the detachment and dissolution of the catalyst from the substrate. In addition, the activity of modified electrode decreases quickly by accumulation of chemisorbed intermediates, which block the catalyst surface. In order to achieve electrode with high sensitivity and long-term stability and to develop a simple method for preparing a modified electrode, sol–gel technique has been developed.[9-16] Now, the sol-gel process conducted in the presence of graphite powder was proposed for the fabrication of carbon ceramic electrodes (CCEs) as a new kind of carbon substrates in electrochemical systems. Considering the stability, permeability, simplicity, versatility, physical rigidity, transparency, porosity, efficient encapsulation, and flexibility in the fabrication procedure of carbon-ceramic substrate, it is one of the best materials that can be used as catalyst supporter. [9, 10] The sol–gel method offers a possibility of preparing glassy material at room temperature that can support the immobilization of different mediators and reagents. These special properties of modified carbon ceramic electrodes (CCEs) have attracted a lot of attention.

Recently, the sol–gel derived ceramic carbon composite electrodes (CCEs) have become increasingly used for the fabrication of effective electrochemical sensors.[9] The composite electrodes are prepared by mixing carbon with the organically modified silicates (or mosils) and the resultant mixture is packed into a tube or spread on a suitable surface. It is therefore possible to dope the ceramic composite with a wide variety of reagents or catalysts to fabricate the desired sensing material.

We recently reported copper chloride[17] and copper bromide [1] modified copper electrodes. In these electrodes, thin films of copper chloride and copper bromide have been deposited on the surface of copper electrode. In continuation of our study to prepare modified electrodes with copper halides and in order to maintain long-term stability, at this study we reported a sol-gel derived ceramic-carbon composite electrode by the use of copper (I) iodide as modifier.

2. Results and Discussion

In this study, CIM-SGD-CCC electrode was prepared and used as a new electrode. Repetitive cyclic voltammograms (CVs) of CIM-SGD-CCC electrode in 0.1 mol L^{-1} NaOH solution in the range of -250 to 1000 mV (vs. Ag/AgCl) at a scan rate of 50 mVs^{-1} have been shown in Fig. 1.

There are prominent peaks during the first cycle. During the next cycles, however, featureless voltammograms were recorded. This indicates that an irreversible electrochemical transformation of the CuI has been achieved during the cyclic voltammetry. It seems that a film of oxy copper iodide is formed at the surface of electrode during the cyclic voltammetry step, according to the following reaction: [1, 17]

$$2CuI + 2OH^- \longrightarrow (ICu)_2O + H_2O + 2e \tag{1}$$

Cyclic voltammetry was used to examine the electro-catalytic efficiency of the CIM-SGD-CCC electrode for the oxidation of hydrazine. Fig. 2 illustrates the CVs of 10^{-3} mol L^{-1} hydrazine at the bare (b) and copper iodide modified (d) sol-gel derived ceramic-carbon composite electrodes in 0.1 mol L^{-1} NaOH solution at 50 mVs^{-1} in a potential range of -250 to 1000 mV versus Ag/AgCl.

At the bare electrode, hydrazine shows a featureless voltammogram. But at the copper iodide modified sol-gel derived ceramic-carbon composite electrode, a large anodic peak appears at 385mV.
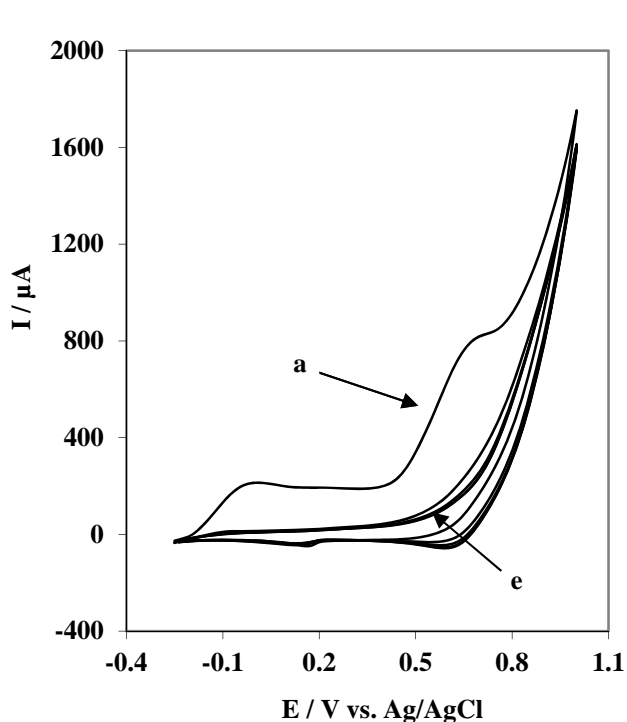

Fig. 1. Repetitive cyclic voltammograms of CIM-SGD-CCC electrode in 0.1 mol L^{-1} NaOH in the potential range of -250 − 1000 mV. Potential sweep rate is 50 mV s $^{-1}$. (a) First cycle; (e) end cycle

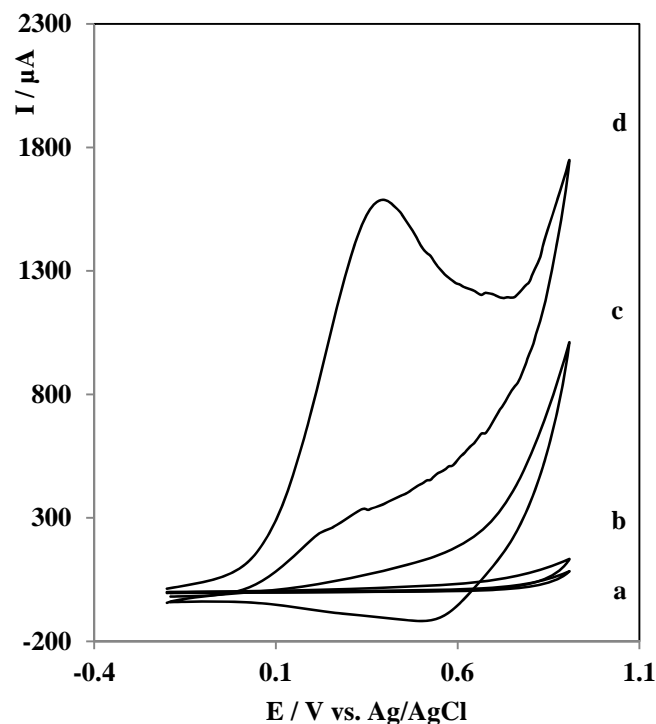**Fig. 2**. Cyclic voltammetric responses of bare sol-gel electrode in 0.1 mol L^{-1} NaOH solution, without (a) and with 10^{-3} mol L^{-1} hydrazine (b). Cyclic voltammograms of CIM-SGD-CCC electrode in 0.1 mol L^{-1} NaOH solution in the absence (c) and presence of 10^{-3} mol L^{-1} hydrazine (d). Conditions: scan rate of 50 mV s^{-1}, potential range -250 − 1000 mV

Comparing (b) and (d) in Fig. 2 shows that at the CIM-SGD-CCC electrode the anodic current of hydrazine oxidation has been greatly enhanced indicating that the anodic oxidation of hydrazine could be catalyzed at CIM-SGD-CCC electrode. This proves that the copper iodide bears the main role in electro-catalytic oxidation of hydrazine. The increased activity probably related to a more favorable adsorption of reactant or of intermediates leading to a higher surface concentration of electroactive molecules ready for being oxidized or it is due to the partial delocalization of the electronic density of hydrazine into the solid with possible consequent bond pre-dissociations which facilitates the oxidation or both.

The amount of copper iodide used for the fabrication of the modified electrode was optimized. The effect of the amount of CuI on the modification process was ascertained by preparation of the modified electrode with various amounts of CuI, and then, by plotting the peak current as a function of CuI amount. Results showed that the oxidation current for 10^{-3} mol L^{-1} hydrazine increases gradually with increasing CuI amount in the range 0.05-0.15 gr and then decreases. Therefore, 0.15gr CuI was selected as optimum level in subsequent studies.

Although the exact mechanism was hard to confirm, the first intermediate of hydrazine oxidation in alkaline solutions seems to be [HO-H$_2$N=NH$_2$-OH]$^{2-}$. Based on the studies reported in literatures [2] the following mechanism can be proposed for the oxidation of hydrazine in alkaline solutions:

$$N_2H_4 + 2HO^- \rightarrow [HO\text{-}H_2N=NH_2\text{-}OH]^{2-} \tag{2}$$
$$[HO\text{-}H_2N=NH_2\text{-}OH]^{2-} \rightarrow N_2H_2* + 2H_2O + 2e^- \tag{3}$$
$$N_2H_2* + 2HO^- \rightarrow N_2 + * + 2H_2O + 2e^- \tag{4}$$

In Eq. (4), the star designates an adsorbed species or a free adsorption site of $(ICu)_2O$. Fig. 3A shows a cyclic voltammogram of the CIM-SGD-CCC electrode at various scan rates obtained in 0.1 mol L^{-1} NaOH containing 10^{-3} mol L^{-1} hydrazine. It can be noted from this figure that, with an increasing scan rate, the peak potential for the catalytic oxidation of the hydrazine shifts to more positive potentials, suggesting a kinetic limitation in the reaction between the redox sites of the modifier and the hydrazine. However, the peak current for the anodic oxidation of the hydrazine is proportional to the scan rate at high scan rates (Fig. 3B); which is an indication of a adsorption-controlled reaction.
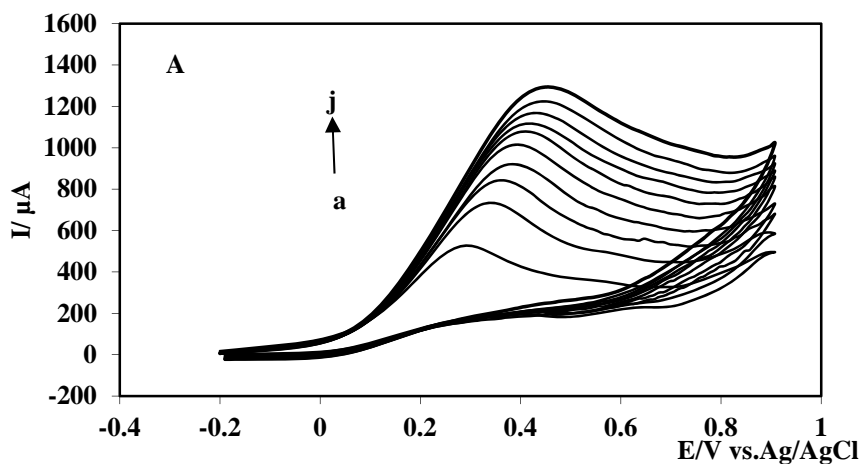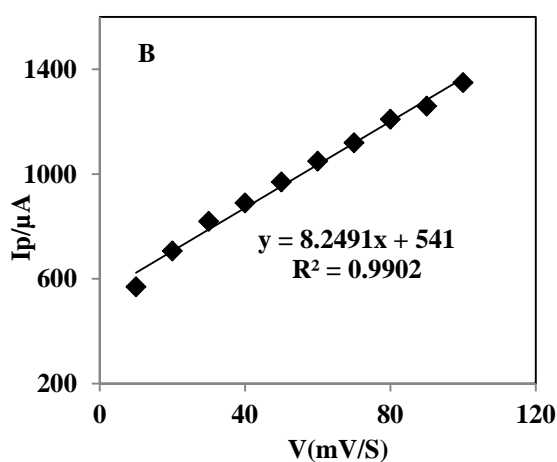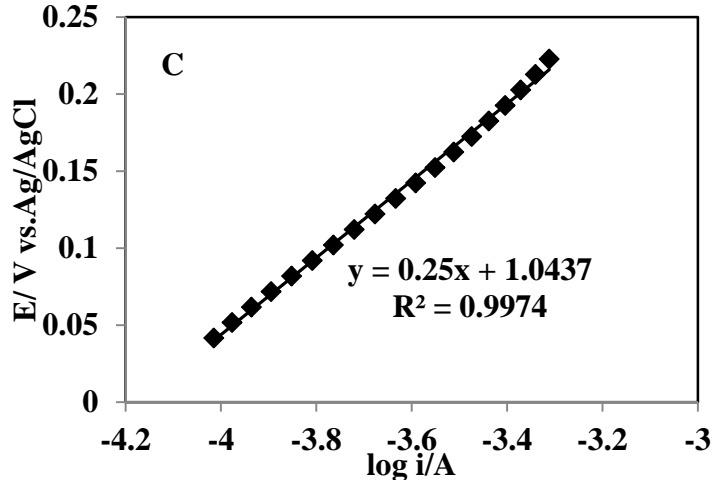

Fig. 3A.

Fig. 3B.

Fig. 3C.

Fig. 3. (A) Dependence of the cyclic voltammetric response at a CIM-SGD-CCC electrode on sweep rate in 0.1 mol L^{-1} NaOH containing 10^{-3} mol L^{-1} hydrazine. (a)– (j): Scan rate: 10, 20, 30, 40, 50, 60, 70, 80, 90, 100 mV s^{-1}. (B) Variation of the catalytic current with the sweep rate. (C) Plot of E vs. log i

To obtain information on the rate-determining step, a Tafel plot (Fig. 3C) was drawn from data of the rising part of the current–voltage curve at a low scan rate of 20 mV s^{-1}. A slope of 199.57 mVdecade^{-1} is obtained indicating the one-electron transfer to be rate limiting assuming an anodic electron-transfer coefficient of $\alpha = 0.76$.

Fig. 4A shows the effect of hydrazine concentration on the cyclic voltammograms of the CIM-SGD-CCC electrode. As can be seen from Fig. 4A, the height of the anodic peak increases with increasing hydrazine concentration. The calibration curve obtained from these voltammograms is shown in Fig.4B. There is a good linear relationship between the oxidation peak current and the hydrazine concentration in the range of 2×10^{-4} to 12×10^{-4} mol L^{-1}.
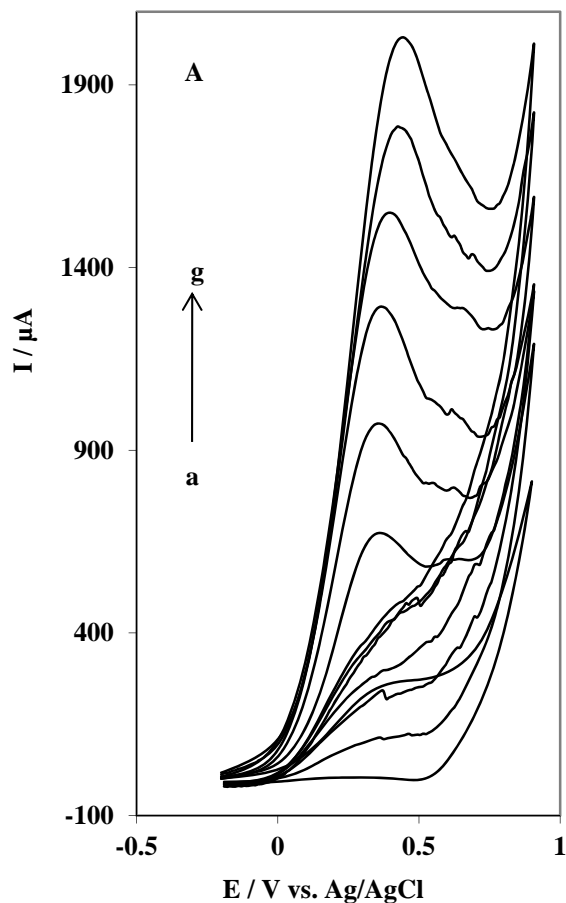
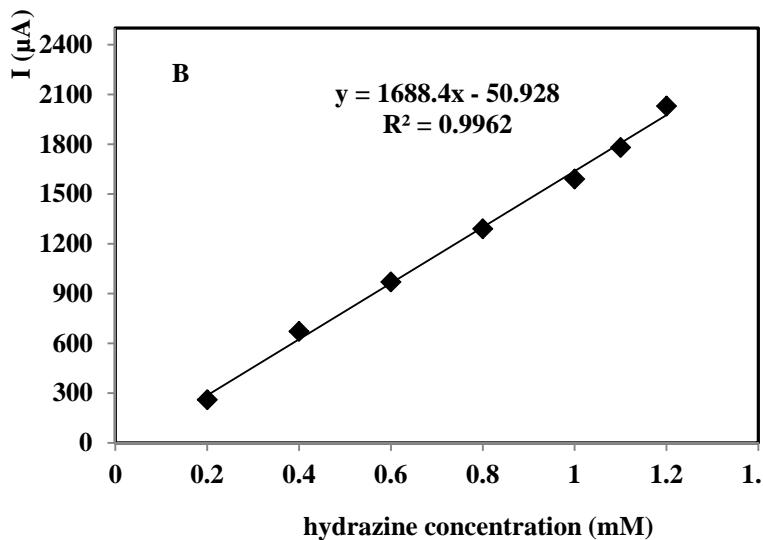**Fig. 4A.**   **Fig. 4B.**

Fig. 4. (A) Cyclic voltammograms of a CIM-SGD-CCC electrode in the presence of various hydrazine concentrations: (a)–(g): 2, 4, 6, 8, 10, 11, and 12 ($\times 10^{-4}$) mol L^{-1} respectively, at a scan rate of 100 mV s^{-1}, in 0.1 mol L^{-1} NaOH solution. (B) Variation of anodic peak current vs. hydrazine concentration
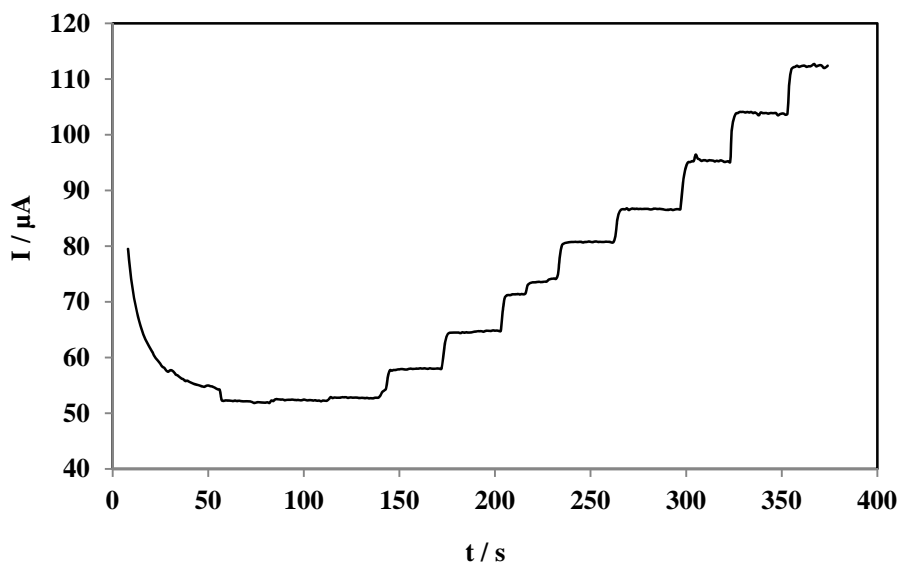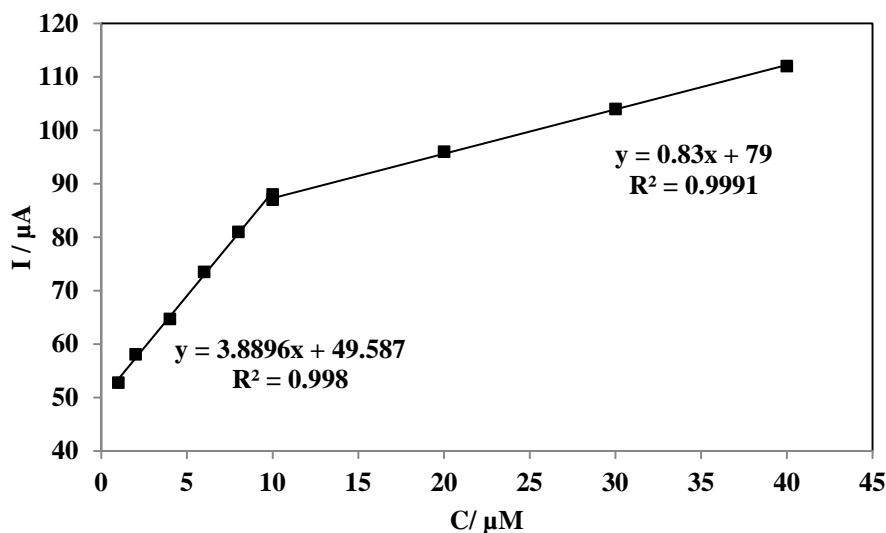

Fig. 5A

Fig. 5B

Fig. 5. (A) Amperometric response of the CIM-SGD-CCC electrode kept in 600 mV in 0.1 mol L^{-1} NaOH, containing different concentrations of hydrazine from 1 to 40 μ mol L^{-1}. (B) Calibration plot for concentrations of hydrazine

Fig. 5A shows the effect of concentration of the hydrazine on the amperograms of the CIM-SGD-CCC electrode when the potential was kept at 0.36 V during the successive addition of hydrazine. Fig. 5B shows that the plot of I_p versus hydrazine concentration between 1 μ mol L^{-1} and 40 μ mol L^{-1} consists of two linear segments with different slopes, corresponding to two different ranges of hydrazine concentration. We ascribe these to a change in the reaction conditions arising from the formation of nitrogen gas bubbles at the surface of the electrode, as has already been reported[8]. Indeed at low concentrations of hydrazine, the gas formed, being negligible has no effect on the diffusion of hydrazine toward the electrode surface. However, at high concentrations of hydrazine, gas evolution at the electrode surface reduces to some extent the normal diffusion of the substrate. The calibration plot gives a limit of detection (LOD) of 0.524 μ mol L^{-1}. The repeatability of the response current of the CIM-SGD-CCC electrode was investigated at various hydrazine concentrations. The relative standard deviation (R.S.D.) was 0.72 % for 5 successive assays.

The influence of a number of potential interferents on the determination of hydrazine was studied under the optimum conditions. The tolerance limit was defined as the maximum concentration of the interfering species that cause an error less than 5% for determination of hydrazine. It was found that 50-fold excesses of Na$^+$, K$^+$, NH$_4^+$, Mg^{2+}, SO$_4^{2-}$, NO$_3^-$, CH$_3$COO$^-$, Cl$^-$, Br$^-$, methanol, ethanol, glucose, lactose and fructose did not interfere with the determination of hydrazine. These results indicate that the CIM-SGD-CCC electrode has good selectivity for the determination of hydrazine.

In order to check the validity of the proposed electrode for the determination of hydrazine, drinking, river and rain water samples were spiked with 20 μ mol L^{-1} of hydrazine and were analyzed under optimized conditions. Acceptable recoveries of hydrazine were obtained with RSDs less than 4% (n = 3).

3. Conclusion

Copper iodide modified sol-gel derived ceramic-carbon composite (CIM-SGD-CCC) electrode was prepared as a new electrode and used for electrocatalytic oxidation of hydrazine. The CIM-SGD-CCC electrode exhibits good electrocatalytic activity towards hydrazine. In comparison with the data on the bare sol-gel derived ceramic-carbon composite electrode, an increase in peak current of

hydrazine was observed at the CIM-SGD-CCC electrode. This proves that the copper iodide bears the main role in electro-catalytic oxidation of hydrazine.

4. Experimental

4.1. Materials and Methods

Hydrazine and other reagents were of analytical grade supplied by Merck (Darmstadt, Germany) and were used without further purification. All solutions were prepared with doubly distilled water. Electrochemical measurements were carried out in a conventional three-electrode cell powered by an electrochemical system comprising an AUTOLAB system with PGSTAT12 boards (Eco Chemie, Utrecht, The Netherlands). The system was run on a PC using GPES 4.9 softwares. CIM-SGD-CCC electrode as working electrode (prepared as follows) was employed for the electrochemical studies. A platinum wire was employed as counter electrode and an Ag, AgCl electrode served as the reference electrode. All experiments were performed at room temperature of 25 ± 2 °C.

4.2. General procedure

The fabrication of CIM-SGD-CCC electrode is described as follows. At the first step a solution of 0.9 ml methanol, 0.6 ml methyltrimethoxysilane (MTMOS), and 0.1 ml hydrochloric acid was mixed and stirred for 2 min to ensure uniform mixing. Then 0.3 g graphite powder and 0.15 g CuI powder were added and the mixture was shaken for an additional 5 min. The mixture was added into Teflon tubes (with 2 mm inner diameter and 5 cm length, and the length of composite material in the tube was about 0.5 cm) and dried for 24h at room temperature. At the second step the electrode was polished with polishing paper. Then, the electrode was placed in 0.1 mol L^{-1} NaOH and the electrode potential was cycled between -250 and 1000 mV (vs. Ag/AgCl) at a scan rate of 50 mVs^{-1} for 5 cycles in a cyclic voltammetry regime until a featureless voltammogram was obtained. Electric contacts were made with copper wire through the back of the electrodes. The electrode was rinsed with distilled water, and applied for electrochemical studies.

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