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A novel sensor based on Ag-loaded zeolitic imidazolate framework-8 nanocrystals for efficient electrocatalytic oxidation and trace level detection of hydrazine

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ABSTRACT

A novel amperometric sensor based on ZIF-8 nanocrystals (Ag/ZIF-8/CPE) was developed to detect hydrazine. Nano-sized ZIF-8 was synthesized via a facile method and its structure was characterized through various techniques such as X-ray diffraction (XRD), scanning electronic microscopy (SEM), Brunauer–Emmett–Teller (BET) and Fourier transform infrared (FT-IR). CPE was then modified with ZIF-8 nanocrystals followed by loading of Ag to fabricate Ag/ZIF-8/CPE. According to cyclic voltammetry results, Ag/ZIF-8/CPE indicated good electrocatalytic activity toward the oxidation of hydrazine. The modified electrode was then applied as a sensor for amperometric detection of hydrazine. The sensor exhibited a wide linear range from 6 to 5000 μM, a low detection limit (S/N = 3) of 1.57 μM, high sensitivity of 54.46 μA mM^{-1} cm^{-2} and a good response time of about 3 s. In addition, the sensor showed high selectivity toward the detection of hydrazine in the presence of some common interferents. The practical application of the sensor was evaluated in different water samples with good recoveries.

1. Introduction

Hydrazine is a reactive molecule with powerful reducing and antioxidant capabilities. Also, it is widely used in various fields, such as fuel cells, catalysts, blowing agents, rocket fuels, heat stabilizers, corrosion inhibition, plutonium extraction and the synthesis of pharmaceuticals and insecticides [1,2]. Despite these advantages, hydrazine as a highly toxic and irritant substance can cause skin corrosion, eye damage, respiratory sensitization, cell mutagenicity and carcinogenicity [3,4]. Therefore, sensitive and selective detection of hydrazine in trace amounts has attracted considerable interests. Hydrazine determination has been carried out by various analytical methods such as titrimetry [5], coulometry [6], amperometry [7], potentiometry [8], spectrophotometry [9] and chromatography [10].

Hydrazine redox process at the surface of ordinary carbon electrodes exhibits high oxidation overpotential which reduces the sensitivity of the electrode. In order to overcome these problems, several electrodes based on metals and nobel metals [11,12], composites [13,14], redox mediators [3,15,16] and pretreated glassy carbon [17,18] have been proposed for electrocatalytic oxidation of hydrazine. These electrodes have their benefits and limitations in terms of linear dynamic range, detection limit and sensitivity. Therefore, efforts are focused on the fabrication of simple, low cost, sensitive and selective modified electrodes for efficient electrocatalytic oxidation of hydrazine.

It has been found that nanostructured materials can decrease the overpotential of the redox process of electroactive species due to their large surface to volume ratio [19]. Nanoporous materials as a subclass of nanostructured materials have been used to fabricate a new type of chemically modified electrodes (CMEs) with rapid electron transfer kinetic [20,21]. Metal-organic frameworks (MOFs) are a new class of crystalline nanoporous materials in which metal ions are bonded by organic linkers [22]. They have unique properties such as high specific surface area (even higher than that of zeolites and activated carbons), porosity and flexibility [23]. Combining these properties with electrocatalytic characteristics of some metals can open a new insight into the field of electrode surface modification to fabricate efficient electrochemical sensors [24]. These sensors have been applied successfully to the detection and determination of some important environmental and biological substances such as hydrogen peroxide, methanol, and hydrazine [25,26]. Nonetheless, the electrochemical application of MOFs is still in its initial steps.

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Zeolitic imidazolate frameworks (ZIFs) as a subfamily of MOFs are constituted by linking four-coordinated transition metals and imidazolate units [27]. ZIFs are used in various fields such as gas adsorption, molecular separation, chemical sensing and catalysis [28,29].

One of the most important primary ZIF members is ZIF-8. ZIF-8 is constructed by linking Zn^{2+} cations and bridging 2-methylimidazolte anions to yield 3D extended tetrahedral framework structure. The angle of Zn-imidazolate-Zn is close to 145°, which resembles zeolite framework [30]. In ZIF-8 large cavities of 11.6 Å diameter are connected through small channels of 3.4 Å diameter [31]. ZIF-8 has several advantages such as high specific surface area, easy activation together with remarkable thermal and chemical resistance to boiling water, organic solvents and alkaline aqueous solutions [32]. In comparison with zeolites, ZIF-8 has more flexible framework and larger pore sizes which is helpful in surface modification; also, it can be synthesized at room temperature without the presence of template [33].

To the best of our knowledge, no modified electrode based on Ag-loaded ZIF-8 has been prepared for electrocatalytic oxidation of hydrazine to date. In the present work, ZIF-8 nanocrystals were applied for the fabrication of a novel hydrazine electrochemical sensor. At first, ZIF-8 nanocrystals were synthesized using a simple method and then Ag/ZIF-8/CPE was fabricated by modification of carbon paste electrode with ZIF-8 and subsequent loading of Ag. The electrocatalytic activity of the sensor toward the oxidation of hydrazine has been assessed by cyclic voltammetry and amperometry. Results showed that the modified electrode has acceptable performances in terms of response time, sensitivity, selectivity and linear range.

2. Experimental

2.1. Chemicals

Zinc nitrate ($Zn(NO_3)_2$), 2-methylimidazole ($C_4H_6N_2$), silver nitrate, hydrazine monohydrate ($N_2H_4{\cdot}H_2O$) (%35), methanol and sodium hydroxide were all purchased from Merck. Graphite powder and paraffin were obtained from Fluka. Double distilled water was used to prepare all solutions.

2.2. Apparatus

In order to characterize ZIF-8 nanocrystals structure, powder X-ray diffraction (XRD) patterns were recorded on a Bruker D8 advance diffractometer employing Cu K_α radiation ($\lambda = 1.5418$ Å) within the 2θ range of 5–40°. Fourier-transform infrared (FT-IR) spectrum was obtained using FTIR spectrophotometer (Vector 22-Bruker) in the range of 3000–400 cm^{-1}. Scanning electron microscopy (SEM; EM-3200, KYKY) was used to determine the size and morphology of the synthesized nanocrystals. Nitrogen adsorption/desorption were performed on a Brunaure–Emmett–Teller (BET, Quantachrome, Nova series). BET surface area, pore volume and pore size were calculated by analysing obtained isotherms.

Cyclic voltammetry and amperometry studies were conducted at room temperature (25 ± 2 °C) using a bipotentiostate/galvanostate (Dropsens, μSTAT 400) equipped with a three electrode cell containing an Ag|AgCl (3 M KCl solution), a platinum wire and a modified CPE as reference, auxiliary and working electrode, respectively. A 0.1 M aqueous solution of NaOH was used as the electrolyte. Prior to each electrochemical experiment, solutions were purged with pure nitrogen for at least 10 min. Electrochemical impedance spectroscopy (EIS) analyses were performed on a potentiostat/galvanostat (Palmsens[3]) using an alternating current voltage of 10 mV over the frequency range of 0.01 Hz to 20 kHz. EIS studies were carried out in a 1:1 mixture of 1.0 mM $K_3Fe(CN)_6/K_4Fe(CN)_6$ as redox probe in 0.1 M KCl solution.

2.3. Synthesis of ZIF-8 nanocrystals

ZIF-8 nanocrystals were synthesized according to the route reported previously with some modifications [32]. The molar ratio of Zn^{2+}: 2-methylimidazole: methanol in synthesized solution was about 1: 4: 1000. For this propose, two solutions, A and B, were prepared: solution A by dissolving $Zn(NO_3)_2$ in methanol and solution B by dissolving 2-methylimidazole in methanol. Then two solutions were mixed under rapid agitation until the mixture turned cloudy. After 12 h, the resultant particles were centrifuged and washed with fresh methanol and then dried in an oven at 80 °C.

2.4. Preparation of carbon paste electrodes

At first, ZIF-8 and graphite powder with a weight ratio of 30:70 were mixed in diethyl ether. Subsequently, with the addition of several drop of paraffin oil, the components were completely mixed to form ZIF-8 modified carbon paste. A portion of the modified carbon paste was packed into the one side of a glass tube with internal diameter of 2 mm. To establish electrical contact, a copper wire was inserted into the tube. The surface of the electrode was then polished to obtain ZIF-8/CPE. Also, CPE as an unmodified electrode was prepared by a similar procedure without the presence of ZIF-8. At the next step, CPE and ZIF-8/CPE were immersed in a 0.1 M AgNO3 solution for 5 min and then washed with double distilled water. These electrodes were then applied as working electrode in a three electrode cell in 0.1 M NaOH solution and potential was set at −1 V vs. Ag|AgCl for 300 s to obtain Ag/CPE and Ag/ZIF-8/CPE. ZIF-8/CPE was used to study the role of ZIF-8 in electrocatalytic oxidation of hydrazine. In order to investigate the tendency of carbon paste to adsorb Ag species, blank experiment was performed using Ag/CPE.

2.5. Voltammetric and amperometric studies

The electrocatalytic behavior of Ag/ZIF-8/CPE toward the oxidation of hydrazine was investigated by both cyclic voltammetry and amperometry in 0.1 M NaOH solutions containing different amount of hydrazine. Also as a reference, the electrochemical behavior of Ag/ZIF-8/CPE was studied by cyclic voltammetry in 0.1 M NaOH solution without the presence of hydrazine.

3. Results and discussion

3.1. Characterization of ZIF-8 nanocrystals

XRD pattern of the synthesized ZIF-8 nanocrystals is presented in Fig. 1A. The peaks are in good agreement with the previous literatures and indicate the formation of pure phase ZIF-8 nanocrystals [34]. Observing well-shaped peaks especially a very sharp peak at 2θ of 7.36° reveals the high crystallinity of the synthesized nanoparticles.

Fig. 1B displays the FT-IR spectrum of ZIF-8 nanocrystals in the range of 3000–400 cm^{-1}. Results confirm that the synthesized sample is ZIF-8 [35]. The peaks at about 2926 cm^{-1} and 1583 cm^{-1} are ascribed to the C—H and C═N stretching of the ring, respectively. The bands in the range of 650 to 1500 cm^{-1} belong to the vibration modes of the imidazolate ring; the signal corresponding to Zn—N bond stretching appears at 421 cm^{-1}.

SEM image of the synthesized sample (Fig. 1C) reveals the formation of spherical-like shape nanoparticles with a size distribution of about 60–90 nm.

Fig. 1D shows the N_2 adsorption/desorption isotherms of ZIF-8 nanocrystals. First step at relatively low pressure is attributed to the presence of micropores at the structure of nanocrystals. A