



Cerium hexacyanoferrate/ordered mesoporous carbon electrode and its application in electrochemical determination of hydrous hydrazine

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ABSTRACT

Via electrochemical polymerization process, cerium hexacyanoferrate/ordered mesoporous carbon modified glass carbon electrode (CeHCF/OMC/GCE) was prepared. The new hybrid material of modified electrode was characterized by cyclic voltammetry (CV) and scanning electron microscopy (SEM), and the as-prepared CeHCF/OMC/GCE was used for the detection of hydrous hydrazine. The results show that the present electrode exhibits some good behaviors such as excellent reproducibility, fast response time, easy preparation, and so on. Under the selected conditions, the linear relationship between the current response and hydrous hydrazine concentration is in the range from 1 to 163 $\mu\text{mol/L}$ with a correlation coefficient of 0.998 ($n = 10$), and the detection limit is 0.1 $\mu\text{mol/L}$ ($S/N = 3$).

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1. Introduction

Many advanced carbon materials, including graphite [1], C_{60} [2], carbon onions [3], carbon nano-crystals (CNCs) [4], single-walled carbon nanohorns (SWCNHs) [5], carbon nanotubes (CNTs) [6], etc. have been applied to construct electro-biosensors. Besides, now a novel carbon material, OMC, has attracted enormous interest, since its first synthesis in 1999 [7]. Due to the advantage of high specific surface area, ordered pore structure, well defined pore size, good conductivity and chemical inertness [8–10], OMC has been widely used in energy storage, capacitors design [11] and to study the electro-catalytic behavior of the substances [12,13].

Hydrous hydrazine is a very important chemical compound with strong reducing ability, which is widely used in industrial applications, such as catalysts, insecticides, antioxidants, textile dyes, photography chemicals, fuel cells and rocket propulsion systems [6,14]. However, the hydrous hydrazine is a toxic material and has negative health effect, and it can cause the diseases such as headache, temporary blindness, DNA damage [15], and even on central nervous system. So the determination of hydrous hydrazine has drawn significant attention, and a reliable and sensitive detection method is highly expected.

Some measurements have been developed to determine hydrous hydrazine, such as spectrophotometry [16], titrimetry [17], chromogenic reaction [18], fluorimetry [19], and so on. By

comparison, electrochemical techniques have become an important method for hydrous hydrazine detection due to its attractive features of rapidity, easy operation procedures, economy of operations and high sensitivity [20]. Nevertheless, direct electrochemical oxidation of hydrous hydrazine is kinetically slow and takes place at a relatively high oxidation potential on common electrodes. An effective way to overcome these difficulties is to use chemical modified electrode [21]. For example, $\text{MnO}_2/\text{MWNTs}$ [22], ZnO/MWCNTs [6], rhodium [14] and Ag–Ni [23] modified electrodes, have been reported for the determination of hydrous hydrazine. Particularly, transition metal hexacyanoferrates (MHCFs) have been used in electrochemistry as electron mediators to transport electrons between analytes and electrodes [24]. Some previous works have been reported about MHCFs to determine hydrous hydrazine, such as nickel hexacyanoferrate (NiHCF) [25] and ruthenium hexacyanoferrate (RuHCF) [26]. However, the oxidation potential of hydrous hydrazine was high and displayed a higher detection limit.

In the present work, cerium hexacyanoferrate (CeHCF), an important analogue of prussian blue (PB), was electrochemically modified on the OMC/GCE to serve as amperometric sensor for hydrous hydrazine. In this structure design, ordered mesopores of OMC will provide easy pathway to disperse CeHCF on its large mesopore surface, increasing CeHCF/electrolyte interface. Furthermore, the new electrode is also more stable with OMC presented [27] and promotes the oxidation current response. Within the present sensor, the oxidation potential of hydrous hydrazine was reduced to 0.34 V and a low detection limit down to 0.1 $\mu\text{mol/L}$ was obtained.

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2. Experimental

2.1. Materials

Hydrous hydrazine ($\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$, 80%) and cerium nitrate ($\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$) were both obtained from Tianjin, China. Potassium ferricyanide ($\text{K}_3\text{Fe}(\text{CN})_6$), hydrochloric acid (HCl) and sodium chloride (NaCl) were both purchased from Beijing Chemical Reagent Co. OMC was prepared according to our previous report [28]. All other chemicals were at least analytical grade.

Water used was doubly distilled through a quartz apparatus. All the solutions were prepared daily and purged with nitrogen. The different pH values of solutions were adjusted with HCl.

2.2. Apparatus

Electrochemical measurements were performed on a CHI660C electrochemical workstation (Shanghai Chenhua Instrument Corporation, China) with a conventional three electrode cell. The modified GCE, an Ag/AgCl electrode (KCl saturated) and a piece of Pt wire were served as working, reference and counter electrode, respectively. SEM images were obtained with a Philips XL-30 ESEM operating at 3.0 kV.

3. Results and discussion

3.1. Preparation of OMC/GCE and CeHCF/OMC/GCE

First, the GCE was polished with 1, 0.3 and 0.05 μm alumina powder, respectively. After rinsed with double-distilled water and ethanol in sonication, 5 μL of the OMC suspension (0.5 mg/mL, in DMF) was cast onto its surface and dried under an infrared lamp for 30 min. Thus OMC/GCE was obtained.

The CeHCF/OMC/GCE was prepared via the following procedure: the same volumes of 1.5×10^{-2} mol/L $\text{K}_3\text{Fe}(\text{CN})_6$, 1.5×10^{-2} mol/L $\text{Ce}(\text{NO}_3)_3$, and 1.5 mol/L NaCl were added into a 10 mL cell to obtain a mixed solution. Then a three-electrode system was set up, the potential cycling was carried out between -0.20 and $+0.80$ V at a scan rate of 100 mV/s under a nitrogen atmosphere. And the cyclic voltammograms (CVs) for the preparation of the CeHCF on the surface of OMC/GCE were shown in Fig. 1. It can be noted that the peak currents decreased slowly with increasing cycle number and well-defined peaks were obtained,

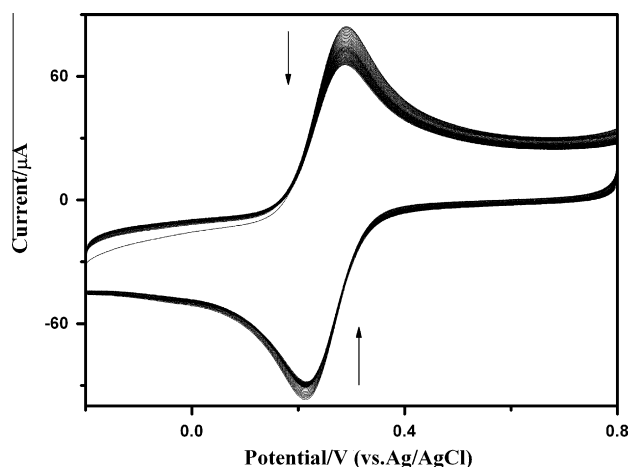


Fig. 1. CVs for the preparation of the CeHCF on the surface of OMC/GCE in a solution containing 1.5×10^{-2} mol/L $\text{K}_3\text{Fe}(\text{CN})_6$, 1.5×10^{-2} mol/L $\text{Ce}(\text{NO}_3)_3$, and 1.5 mol/L NaCl. Scan rate: 100 mV/s.

which indicates the formation of CeHCF film [27]. Following the same procedure, the CeHCF/GCE was prepared.

It is well known that the thickness of the film will define the sensor response, and the film thickness can be estimated by the number of electro-polymerization cycles performed [29]. In the present work, the CeHCF film thickness was approximated by investigating the peak currents of CeHCF/OMC/GCE electro-polymerized from different cycle numbers in 1.5 mol/L NaCl. And the voltammetric response increased with the increasing cycle numbers until at 40 cycles and then decreased slowly (data was not shown). Thus, 40 cycles were selected for electro-polymerization of CeHCF in our experiment.

3.2. Morphology of OMC and CeHCF/OMC

The morphology of CeHCF polymerized onto the OMC surface was first characterized by SEM. Fig. 2 is the SEM images of: (A) OMC and (B) CeHCF/OMC. It can be observed from Fig. 2A that the surface of OMC is a well-defined morphology, and the OMC exhibits the form of small bundles and uniform dispersion. For comparison, Fig. 2B illustrates the morphology of CeHCF polymerized onto the OMC/GCE. It can be seen that the OMC is partially coated by CeHCF. However, the structure of OMC was not changed. Thus, we could confirm that CeHCF was successfully electro-polymerized onto the OMC/GCE.

3.3. Optimization of conditions

To maintain charge neutrality, reversible intercalation and deintercalation of charge-compensating alkali cations take place in the CeHCF electrochemical redox reaction [30]. Fig. 3A shows the voltammetric response of CeHCF films in 1.5 mol/L KCl (curve 1) or NaCl (curve 2) aqueous solution at a scan rate of 50 mV/s. As can be seen, a well-defined peak with a large peak current can be obtained in 1.5 mol/L NaCl compared with KCl, which is accordance with the previous literature [31]. As a consequence, NaCl was chosen as the supporting electrolyte in the present work.

Fig. 3B displays the CVs of CeHCF/OMC/GCE in the solution containing different concentrations of NaCl. It could be found that the peak currents varied with the NaCl concentration and a well current response can be obtained in 1.5 mol/L NaCl. So it is deduced that 1.5 mol/L NaCl is more suitable for the operational requirements of the CeHCF sensors.

In addition, the influence of pH to the film of CeHCF also was investigated. And the CVs of CeHCF/OMC/GCE in 1.5 mol/L NaCl at different pH values (4.0–9.0) were recorded. The peak current gradually enhanced with the pH increased and reached the maximum at pH 7.0, and then gradually decreased, which was most possibly attributed to the formation of $\text{Fe}(\text{OH})_3$ in solution [32]. Owing to a well-defined peak and good voltammetric response can be obtained at pH 7.0, the solution pH of 7.0 was selected in the following experiments.

3.4. Kinetic characteristics of the CeHCF/OMC

Fig. 4A exhibits the CVs of the bare GCE (curve 1), OMC/GCE (curve 2), CeHCF/GCE (curve 3) and CeHCF/OMC/GCE (curve 4) electrodes in 1.5 mol/L NaCl. As seen, there are no obvious peaks at bare GCE and OMC/GCE (curves 1 and 2), but a pair of quasi-reversible redox peak can be observed at CeHCF/GCE (curve 3) and CeHCF/OMC/GCE (curve 4). It can also be noted that the peak current of CeHCF/OMC/GCE (curve 4) is larger than that of CeHCF/GCE (curve 3), confirming that the presence of OMC improves the charge transfer of CeHCF due to the existence of a large amount of edge-plane-like defective sites in the OMC materials and high surface area of OMC [33].

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