Sensors and Actuators B 214 (2015) 132–137

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

journal homepage: www.elsevier.com/locate/snb

Simultaneous determination of hydrazine and hydroxylamine based on fullerene-functionalized carbon nanotubes/ionic liquid nanocomposite

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ARTICLE INFO

Article history:
Received 15 December 2014
Received in revised form 22 February 2015
Accepted 3 March 2015
Available online 18 March 2015

Keywords:
Fullerene
Functionalized carbon nanotube
Ionic liquid
Hydrazine
Hydroxylamine

ABSTRACT

The electrocatalytic oxidation of hydrazine and hydroxylamine were investigated by a fullerene (C_{60})-functionalized carbon nanotubes (CNTs) and Ionic liquid (IL) modified glassy carbon electrode. The physico-chemical properties of catalyst materials were characterized by transmission electron microscopy, scanning electron microscope, electrochemical impedance spectroscopy and voltammetry. The results show that, at the modified electrode surface, the peaks of hydrazine and hydroxylamine oxidation were clearly separated from each other with a potential difference of 450 mV between them. These conditions are sufficient to allow determination of hydrazine and hydroxylamine in the samples at a C60-functionalized CNTs and IL nanocomposite (C_{60}–CNTs/IL/GCE). The electrocatalytic currents increase linearly with the hydrazine and hydroxylamine concentrations in the ranges of 0.05–700.0 and 1.0–300.0 μM, and the detection limits for hydrazine and hydroxylamine, were 17 ± 2 and 28 ± 2 nM, respectively. C_{60}–CNTs/IL/GCE was satisfactorily used for simultaneous determination of spiked hydrazine and hydroxylamine in two water samples.

1. Introduction

Hydrazine and hydroxylamine are two important compounds in chemical industry. Hydrazine has garnered much attention due to its many applications in various fields, including fuel cells, industrial, agricultural, pharmacological, military and aerospace applications [1,2]. Even though hydrazine and its derivatives are widely used for several important applications, they are considered toxic by Environmental Protection Agency (EPA) and the maximum recommended value in trade effluents is set to be 1 ppm [3]. The lungs, liver, kidney, and central nervous systems of living organisms can be injured if hydrazine is inhaled or introduced to the skin. Serious effects on the reproductive system are observed in animals after hydrazine inhalation. These effects have included reduced ovary and testes size and decreased sperm production [4]. Also, hydrazine has been identified as a carcinogenic agent [5]. Hydroxylamine, a derivative of ammonium is one of the reducing agents widely used in industry and pharmacy. It is identified as a key intermediate in the nitrogen cycles and production of nitrous oxide [6]. Hydroxylamine is a well-known mutagen, which induces highly specific mutations with the nucleic acid cytosine. Modest levels of hydroxylamine can be toxic to humans, animals and even plants [7]. Also, in industrial standpoint, it can be used as a raw material for the synthesis of pharmaceutical intermediates and final drug substances.

Therefore, from the industrial, environmental and health viewpoints, development of a sensitive analytical method for the simultaneous determination of hydrazine and hydroxylamine is very important. Electrochemical methods are practical and attractive because electrochemical instrumentation is usually compact, relatively inexpensive, reliable and sensitive [8–10]. Moreover, the development of a rapid electrochemical method for hydrazine and hydroxylamine determination that does not require sample pretreatment is possible. It is known that at a bare electrode surface, the oxidation peaks of hydrazine and hydroxylamine are nearly at the same potential, which results in an overlapped voltammetric response making their discrimination highly difficult. In addition, the electrochemical oxidation of hydrazine and hydroxylamine at bare electrode surfaces requires high-overpotential [11,12].

Carbon nanotubes (CNTs) continue to receive considerable attention in [13–15] CNTs have been the subject of numerous investigations in chemical, physical, and materials areas due to their novel structural, mechanical, electronic, and chemical properties

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http://dx.doi.org/10.1016/j.snb.2015.03.010
0925-4005/

[16]. Chemical and physical functionalization endows CNTs with diverse functions and paves the way for their future applications in different fields [17–19]. Recently, we have successfully introduced benzofuran derivative onto CNTs and used for the electrochemical detection of isoproterenol and serotonin with high specificity and sensitivity [20]. Fullerene science is one of the fastest growing areas of research and its application can be useful for electrocatalysis [21–23]. Fullerene have attracted numerous interests for modifying electrode surfaces because it is chemically stable, metallic impurity free and relative simple to implement and gives rise to reproducible electrocatalytic responses [24]. Due to the rich electrochemical properties of electrochemistry of C_{60}-functionalized CNTs films was investigated since synthesis of fullerene peapods was reported [25]. Carbon nanotubes have also been applied for this purpose because of their remarkable electrocatalytic properties [12]. As an excellent electron acceptor, C_{60} could be dispersed in nanomaterial, such as carbon nanotubes, to facilitate electron transfer. Recent investigations revealed that C_{60}-functionalized CNTs films were found to be electrocatalytic for a range of analytical targets [26–28]. We have recently reported the electroanalytical applications of C_{60}-functionalized CNT composite for the electrocatalytic determination of catecholamines [29].

A few articles have introduced different modified electrodes that can be used for simultaneous oxidation of hydrazine and hydroxylamine [30]. In this paper, we present a C_{60}-functionalized CNTs/IL (1-butyl-3-methylimidazolium tetrafluoroborate) nanocomposite for the simultaneous determination of hydrazine and hydroxylamine. The main object of this work was to develop a method with the capability of separating the electrochemical responses of hydrazine and hydroxylamine simultaneously. This demonstrates that C_{60}-CNT/IL nanocomposite facilitates electron transfer on surface of the electrode due to unique electrochemical properties and ionic liquid has exhibited some advantages including high ionic conductivity, wide electrochemical windows and good solubility, which results in the enhanced sensitivity and stability.

2. Experimental

2.1. Apparatus and chemicals

The electrochemical measurements were performed by an Autolab potentiostat/galvanostat (PGSTAT-302N, Eco Chemie, Netherlands). A three-electrode system was used, where a GCE or a modified GCE served as the working electrode, a platinum wire as the counter electrode and an Ag/AgCl/KCl (3.0 M) electrode as the reference electrode. All potentials reported were versus the Ag/AgCl. A Metrohm 691 pH/Ion Meter was used for pH measurements.

The morphology of nanomaterial was characterized using scanning electron microscopy (SEM, Hitachi S-4160) and transmission electron microscopy (TEM) (Philips EM208). Electrochemical impedance spectroscopy (EIS) measurements were carried out in the presence of 1.0 mM $[Fe(CN)_6]^{3-/4-}$ redox probe prepared in 0.1 M KCl, in a frequency range from 0.01 Hz to 100 kHz at a dc potential of +0.13 V. Differential pulse voltammetry (DPV) was recorded under modulation amplitude of 50 mV.

All solutions were freshly prepared with double distilled water. 1-butyl-3-methylimidazolium tetrafluoroborate and fullerene-C_{60} (99.5%) were reagent grade from Sigma Aldrich. Hydrazine, hydroxylamine, phosphate salt, sodium hydroxide, solvents and reagents were of pro-analysis grade from Merck (Darmstadt, Germany). These chemicals were used without further purification. The multi-wall carbon nanotubes (Outer diameter: 5–20 nm; Inner diameter: 2–6 nm; length: 1–10 μm and 95% pure) were purchased from Plasma Chem (Germany).

2.2. Preparation of the electrode

The modified electrodes were prepared by a simple casting method. Prior to the surface coating, the GCE was polished on a polishing cloth with alumina powder. Purified MWCNTs and C_{60} (MWCNTs/C_{60} = 2:1) with a total amount of about 1 mg were dispersed in 10 mL toluene in an ultrasound bath for 30 min to give a 0.1 mg mL^{-1} suspension. A volume of 10 μL of the suspension was applied directly on a GCE surface and the solvent was allowed to evaporate at room temperature. This C_{60}-MWCNT film electrode was subjected to potential scanning in acetonitrile solution containing 0.1 M tetrabutylammonium hexafluorophosphate between 0.0 and −2.0 V (vs Ag/AgCl) until reversible multistep electron-transfer reaction was obtained [25]. The resulting C_{60}-CNTs film electrode was then washed with acetonitrile several times to remove the electrolytes and dried at room temperature. Then, a 50 μL of IL was dispersed in 0.5 mL 1% chitosan solution in 1 M of acetic acid. After the mixture was sonicated for 30 min, its 3.0 μL was dropped on the surface using a microsyringe and dried in a stream of hot air, which was similar to our group's previous work [29].

For comparison, C_{60}-CNT modified GCE (C_{60}-CNTs/IL/GCE) without IL, CNT and IL modified electrode (CNT/IL/GCE) without C_{60}, CNT modified electrode (CNT/GCE) without IL and C_{60} were also prepared in the same way.

3. Results and discussion

3.1. Characterization of the C_{60}-CNT/IL composites

The response of a modified electrode is related to its physical morphology of its surface. TEM was performed to the C_{60}-CNT composites and it was indicated that C_{60}-CNT composites were obtained under our experimental conditions. As the TEM image in Fig. 1A shows clearly, the C_{60}-CNT composite film comprises small nanoparticles of C_{60} uniformly dispersed on the CNTs. Typical SEM images of C_{60}-CNT and C_{60}-CNT/IL were shown in Fig. 1B and C, respectively. The C_{60}-CNT is characterized by a surface formed by irregularly shaped of CNTs that were isolated and each CNTs could be clearly distinguished (Fig. 1B). When IL is introduced in the C_{60}-CNTs composite further, the film becomes more uniform and even, this is related to the binding and blanketing effect of IL (Fig. 1C). We also added the resulting C_{60}-CNT composites into toluene and subjected the suspension to ultrasonication for several hours, but the toluene solution did not turn purple, a characteristic color of C_{60}. These results indicate that C_{60} has been strongly bounded with CNTs.

3.2. Electrochemical oxidation of hydrazine at various modified electrodes

To evaluate the electrocatalytic behavior of modified electrode towards hydrazine oxidation, cyclic voltammograms at bare GCE (a), CNT/GCE (b), C_{60}-CNTs/GCE (c) and C_{60}-CNTs/IL/GCE (d) were recorded at 50 mV s^{-1} in phosphate buffer solution (pH 7.0) in the presence of hydrazine (Fig. 2A). At bare GCE, only a very small oxidation peak current was observed at about 790 mV (a), while the corresponding potential at C_{60}-CNTs/IL/GCE (d) electrode is 380 mV (d). These results indicate that the peak potential for hydrazine oxidation at the C_{60}-CNTs/IL/GCE (d) shifted approximately 380 mV toward negative values compared to unmodified GCE. The comparison of the oxidation of hydrazine at C_{60}-CNTs/IL/GCE (d) and C_{60}-CNTs/GCE (c) shows an enhancement of the anodic peak current, suggesting IL was beneficial to the electrons transfer [9].

To investigate the roles of C_{60} on CNT surface in the electrochemical oxidation of hydrazine, the CVs of hydrazine at the CNT/GCE