Materials Science and Engineering C 35 (2014) 8–14

Contents lists available at ScienceDirect

Materials Science and Engineering C

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

Construction of a carbon ionic liquid paste electrode based on multi-walled carbon nanotubes-synthesized Schiff base composite for trace electrochemical detection of cadmium

Abbas Afkhami [a,*], Hosein Khoshsafar [a], Hasan Bagheri [b], Tayyebeh Madrakian [a]

[a] *Faculty of Chemistry, Bu-Ali Sina University, Hamedan, Iran*
[b] *Chemical Injuries Research Center, Baqiyatallah University of Medical Sciences, Tehran, Iran*

ARTICLE INFO

Article history:
Received 11 July 2013
Received in revised form 10 October 2013
Accepted 19 October 2013
Available online 31 October 2013

Keywords:
Modified carbon paste electrode
Cadmium determination
Multi-walled carbon nanotubes
Ionic liquid
Anodic stripping voltammetery

ABSTRACT

A simple, highly sensitive and selective carbon nanocomposite electrode has been developed for the electrochemical trace determination of cadmium. This sensor was designed by incorporation of multi-walled carbon nanotubes (MWCNTs) and a new synthesized Schiff base into the carbon paste ionic liquid electrode (CPE_{IL}) which provides remarkably improved sensitivity and selectivity for the electrochemical stripping assay of Cd(II). The detection limit of the method was found to be 0.08 μg L^{-1} (S/N = 3) that is lower than the maximum contaminant level of Cd(II) allowed by the Environmental Protection Agency (EPA) in standard drinking waters. The proposed electrode exhibits good applicability for monitoring Cd(II) in various real samples.

1. Introduction

Cadmium has been recognized as a harmful environmental pollutant known to produce highly toxic effects on different organs and systems of both humans and animals [1,2]. The maximum contaminant level (MCL) allowed by the American Environmental Protection Agency (US EPA) in standard drinking water is 10 μg L^{-1} to provide sample protection of human health [3]. Because of the increasing industrial use of cadmium, in one aspect and its serious hazardous effects on human health, on the other hand, extensive studies have been carried out on the development of methods for Cd(II) determination. Therefore, it is desired to develop simple, selective, efficient and eco-friendly methods for the determination of Cd(II) in environmental and biological samples [4–8]. Although AAS, ICPMS, ICP-OES, etc., are accurate methods for the determination of cadmium, these methods involve high cost for instrumentation and maintenance, time-consuming and less efficiency, and are unfit for rapidly monitoring heavy metals for the characterization of contaminated sites. Electro-analysis, particularly stripping analysis, is the most widely used alternative method. Anodic stripping voltammetry (ASV) is the most attractive electrochemical technique for the determination of trace heavy metals due to its high sensitivity and selectivity. An additional advantage of ASV over the other mentioned methods is the simplicity of the required instrumentation, which is relatively inexpensive, low electrical power consumption, portable as well as suitable for automation [9–11].

In general, the performance of ASV is strongly affected by the electrode materials. An ideal electrode should possess capabilities such as low ohmic resistance, chemical and electrochemical inertness, good mechanical properties, high hydrogen and oxygen overpotential (wide potential window), low background current and ease of reproduction of the electrode surface. Mercury based electrodes have been most widely used in ASV of Cd(II) due to their wide potential window toward negative potential values. However, the recent trends toward green chemistry aim to reduce and to eliminate use of mercury [12,13]. Consequently, various materials have been recently tested as alternative electrodes for ASV of Cd(II), such as bismuth, bismuth film, gold, silver, antimony film and boron-doped diamond [14].

Since its first reporting in 1958 by R.N. Adams, carbon paste electrodes (CPEs) have become widely used in electrochemical research [15,16]. Many factors have led to their popularity, including low ohmic resistance, large potential window, and ease of modification [17].

However, the main challenge is how to improve the selectivity of the electrodes for the determination of a specific metal ion. In order to meet this requirement, preparation of the electrodes inducing metal ion-specific functional groups with the desired properties is particularly attractive. Chemically modified electrodes (CMEs) are one of interesting tools, because they can exert more direct control over the chemical nature of an electrode [10,18]. The main reasons for modifying the electrode are to decrease the detection limit by accumulating the analyte at the electrode surface but still preserve its

---

* Corresponding author. Tel./fax: +98 811 8272404.
E-mail address: afkhami@basu.ac.ir (A. Afkhami).

0928-4931/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.msec.2013.10.025

electroactivity, to generate or increase the electrochemical response and/or decrease the overpotential using electrocatalysts, to shift and separate otherwise overlapping signals, and to improve the general analytical conditions [19–21]. When only the chemical reactions are expected, the modifier should not be electroactive in the potential range of interest. The operation mechanism of such CMEs depends on the properties of the applied modifier(s) that affect its selectivity towards the target species. Modifiers should be rather insoluble in all solutions to which the sensor will be exposed in order to avoid the "bleeding" of the electrode, although adsorption at the carbon particles may also sometimes prevent this undesired effect [18].

Ease of modification is one of the most valuable features of CPEs. This is due to the well-developed surface of CPE, which has a high adsorptivity for substances. Modification of CPEs can be achieved through a multitude of methods. A few of these methods are chemical pretreatment where the carbon is soaked in the modifier and then evaporated to dryness before being prepared as an electrode; in situ modification where the modifier adsorbs at the surface of plain CPE, thus allowing for determination of analyte in the solution [22]; dissolution in the binding liquid which is typically achieved through the use of an ion-exchange resin; or direct mixing of dry modifiers into the paste through mechanical means which is the most frequently used method [17,18,22].

The key point to obtain a good and reliable electrochemical sensor is the kind of materials that constitutes the electrode composite. New types of carbon paste mixtures are under investigation. Traditional CPEs are being replaced by alternate materials. Classical forms of graphite moiety are replaced by new carbon materials like fullerenes, hollow carbon fibers, or carbon nanotubes [23], and traditional pasting liquids are substituted by room-temperature ionic liquids (RTILs) or other recently synthesized organic liquids [24]. The novel properties of nanomaterials make them extremely attractive for electrochemical sensors in comparison to conventional materials. The MWCNTs have been used due to their special physicochemical properties such as ordered structure with high aspect ratio, ultra-light weight, high mechanical strength, high electrical conductivity, high thermal conductivity, metallic or semi-metallic behavior, and high surface area [25–28].

In the past years, as a new "green" media, room temperature ionic liquids (RTILs) have emerged as a frontier and novel area of research because of their excellent chemical and physical properties such as high chemical and thermal stability, ionic nature, good extraction ability, ion-exchange properties, low equilibrium vapor pressure, high conductivity and wide electrochemical windows [29,30]. RTILs have been proposed as efficient pasting binders in place of non-conductive organic binders for the preparation of carbon composite electrodes [25]. These ionic liquid modified carbon electrodes show some advantages over traditional CPEs, such as high conductivity and sensitivity, fast electron transfer and good antifouling ability for electroanalysis. Moreover, the combination of such materials with specific ligands can provide excellent electrochemical platforms for heavy metal analyses due to the combination of the enlarged active surface area, strong adsorptive capability of the nanomaterial and the specific complexing ability of the ligands [31–33]. Therefore, the fabrication of carbon nanotube/ionic liquid paste electrodes is attractive.

Finally, selectivity of the determination of the metal ions was improved by their complexation or chelation with specific ligands [34–38]. 4-((1H-1,2,4-triazol-3-ylimino)methyl)phenol (L) (Scheme 1) is a new synthesized Schiff base. It is capable to form complexes with target ions.

Herein, we report the construction of a nanocomposite electrode based on the L/multi-walled carbon nanotubes (MWCNTs) incorporated into the carbon ionic liquid paste (L/MWCNTs/CPE_{IL}) for the differential pulse anodic stripping voltammetry (DP-ASV) of Cd(II) through cooperative Cd(II)-modifier interactions. It was concluded that this electrode can act as electrochemical cadmium sensor with good reproducibility over a period of several months. The analytical application of the developed sensor has been shown by determining the cadmium ions in different environmental, biological and food samples with complex matrices.

2. Experimental

2.1. Apparatus

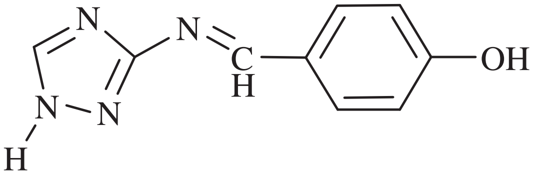
Voltammetric systems were conducted using the Metrohm model 797 VA Computrace polarography (Herisau, Switzerland). Three-electrode cell systems were used to monitor the differential pulse voltammograms. The electrochemical cell was assembled with a conventional three-electrode system, an SCE reference electrode (Azar electrode, Iran) and a platinum wire as a counter electrode. Different working electrodes used in this study were a CPE and different modified CPEs. The cell was a one-compartment cell with an internal volume of 20 mL. All experiments were typically conducted at room temperature. Differential pulse voltammetry was applied for the determination of Cd(II) under the optimized conditions (pulse amplitude, 200 mV; pulse time, 60 ms). A Metrohm model 713 pH-meter (Herisau, Switzerland) with a combined glass electrode was used for pH controlling, and a Heidolph type of stirrer (MR 2000, Kelheim, Germany) was used for stirring the solutions.

2.2. Reagents and materials

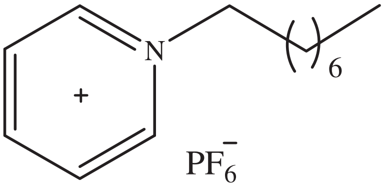
All chemicals used were of analytical grade or of the highest purity available. Cadmium nitrate, and other metal salts were obtained from Merck (Germany) and used as received. Octylpyridinum hexafluorophosphate, IL, (Scheme 2), and graphite powder (mesh size < 50 μm) were supplied by Fluka (Switzerland). All other chemicals were of analytical grade from Merck. The MWCNTs with outer diameter: 5–20 nm; inner diameter: 2–6 nm; length: 1–10 μm and with 95% purity were purchased from Plasmachem GmbH (Germany, www.plasmachem.com). The new Schiff base was synthesized and applied in the composition of modified electrode. Deionized distilled water was used for preparation of all solutions.

2.3. Synthesis of Schiff base

The Schiff base L was synthesized according to the literature [39]. A solution of 3-amino-4H-1,2,4-triazole (2 mmol) in C_2H_5OH (10 mL) was treated with salicylaldehyde in a molar ratio of 1:1.3 and the resulting mixture was acidified by 37% hydrochloric acid (4 drops). The reaction mixture was refluxed for 8 h. The solid residue was filtered and washed with cold solvent.



Scheme 1. Structure of 4-((1H-1,2,4-triazol-3-ylimino)methyl)phenol.



Scheme 2. Structure of octylpyridinum hexafluorophosphate.