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Review

Electrochemical sensors based on polydiaminonaphthalene and polyphenylenediamine for monitoring metal pollutants

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ABSTRACT

In the past few years, many researches have been devoted to electrochemical sensors based on electrode modified with conducting polymers. The combination of carbon electrode and conducting polymers provide extrordinary properties in term of conductivity and electrochemical sensing. In this review, we focus first on synthesis and charaterisation of polyphenylenediamine and polydiaminonaphthalene and their substituted composites prepared on different electrodes with a particular attention to carbon paste electrode. Then, the recent developments of potential application of these sensors in the environmental monitoring will be highlighted.

Contents

1. Introduction

The release of different pollutants into environment has increased noticeably as a result of industrialization, and thereby lowered the quality of the environment. Of such pollutants, the heavy metals are considered to be one of the main sources of pollution in the environment. Besides the fact that some heavy metal ions are essential to many organisms in small doses, high doses affect the ecosystem and human health. However, excessive levels or even small doses of very toxic metals (i.e. lead, cadmium, mercury) can cause several damages on the environment and human health [1,2]. Therefore sensitive and selective methods for the detection of heavy metals have become a priority in environmental monitoring [3]. Electrochemical methods compared to standard spectroscopic techniques, such as atomic absorption spectrometry (AAS) and inductively coupled plasma optical mass spectrometry (ICP-MS) offer several advantages related to their cost, simplicity and the possibility of in-field application. Among the different electrochemical techniques, voltammetric and potentiometric techniques using chemical sensors are the most reported for heavy metals detection [4,5]. Different electrochemical techniques used for the detection of heavy metals in environment samples using different electrodes which have demonstrated great potential as effective tools [6–10]. In comparison with membrane electrodes, carbon paste electrodes (CPES) as ion selective electrodes have gained considerable attention mainly due to their advantages such as renewability, stable response, low ohmic resistance, no need for internal solution

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[4,11–18]. The introduction of a chemical modifier, which is able to preconcentrate metallic ions on the electrode surface by either complexation or electrostatic attraction, can lead to more sensitive electroanalytical procedures with lower detection limit values.

CPEs under the field of chemically modified electrodes (CMEs) can be easily modified by being mixed with various modifiers depending on the application. They further offer a renewable and modified surface, are cheap, and offer very low background current interferences [19–24]. The voltammetric determination of various trace metals after their preconcentration at CMEs received a high interest as a research area. Several modifiers have been used in the construction of CMEs. The commonly used are organic polymers [25–31]. Such modified electrodes can significantly improve the electrocatalytic properties of substrates, decrease the overpotential, increase the reaction rate and improve the stability and reproducibility of the electrode response. The modification of the electrode by organic conducting polymers has been a very active area of research. Organic conducting polymers, born in 1977, with the pioneering work of MacDiarmid, have received great attention due to their potential application [32]. Intensive research has been devoted to preparation and characterization of conducting polymers such as polyaniline, polypyrrole, polydiaminonaphthalene and their derivatives. Their high application potential in different field as batteries, sensors, capacitors or electrochromic displays; explain the intensive investigation of the conducting polymers [33,34]. During the last decades, different approaches have been used to develop high-performance electrochemical sensors based on conducting polymers [35,36]. More than 20,000 papers have been devoted to the synthesis, characterization and application of conducting polymers between 2007 and 2013 in which about 5000 papers are specific to phenylenediamine (PD) and diaminonaphthalene (DAN). Aromatic amine conducting polymers are mainly organic compounds that have extended single and double bonds alternating in a π–orbital system. The electrons can be transferred along polymer chains. The electrical properties of these polymers can be reversibly modulated by doping and undoping processes.

In recent years, it is found that the conducting polymers from aromatic diamines have a unique ability to form stable complexes with some heavy metal ions such as Pb(II), Hg(II) and Ag(I) ions [37–42]. In addition to the many important applications of the aromatic diamines polymers described in the literature, it was found that the oxidation reactions of aromatic diamines are also very essential in several application fields including biosensors, the immunosorbent assay, detection of hemoglobin and H_2O_2, determination of traces of metal ions, and electrocatalysis [43–47] as shown in Fig. 1.

The aim of this review is to cover particular aspects related to polydiaminonaphthalene [poly(DAN)] and polyphenylenediamine [poly(PD)] prepared on different substrate, their characterization and strategies applied to improve their properties. We will also discuss their application as electrochemical sensor for monitoring metals pollutants.

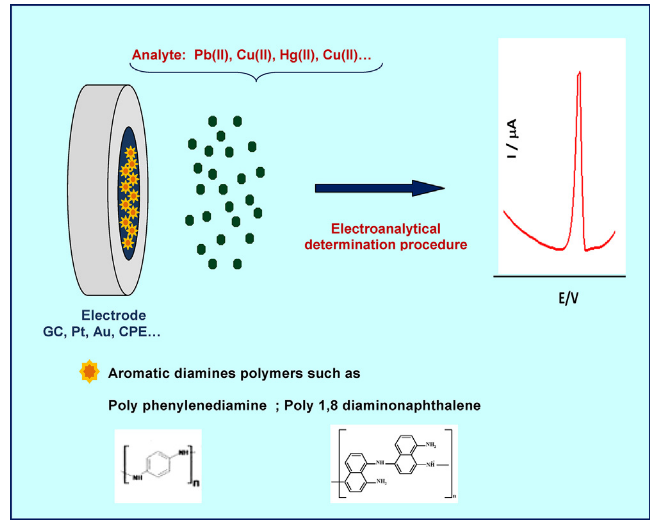

Fig. 1. Schematic of electrochemical sensor based on conducting polymers. A chemical sensing elements detect a specific analyte producing an electronic signal (peak current is the case of stripping analysis) that is proportional to the concentration of analyte.

2. Synthesis and characterization of diaminonaphthalene on solid electrode

Different methodologies have been used to prepare polymeric films modified electrodes. Among them, electropolymerization has demonstrated to be a very convenient means for immobilizing polymers on various conductive substrates because the deposition can be controlled by adjusting the electrochemical parameters and the process is located at the electrode surfaces. This new class of the electrode material has been found to improve the electrode sensitivity and selectivity and to reduce fouling effects in many applications [48–57]. The chemical and electrochemical deposition of diaminonaphthalene has been widely studied by different authors. Generally, electropolymerization of DAN is performed in an electrochemical cell by using a three-electrode system consisting of working, counter, and reference electrodes. The working electrode was immersed in a solution containing monomer and supporting electrolyte both dissolved in an appropriate amount. Then electropolymerization is carried out by cyclic voltammetry, potentiostatic or galvanostatic mode. It has been reported that among many isomers of DAN can electropolymerize. Each polymer has its own individual structure and characteristics. With different electropolymerization conditions, polymer films with various properties are electrodeposited from different solutions onto different electrodes [38]. Electropolymerization of 1,5- or 1,8-diaminonaphthalene in acetonitrile solution was reported in the literature [58,59]. Oxidative polymerization of 1,5-DAN has been carried out on platinum and carbon graphite electrode by cyclic voltammetry and controlled potential, the electrical conductivity of the film was measured [60]. Oyama et al. [61] polymerize 1,8-DAN by anodic oxidation in both acidic and acetonitrile solutions. The resulting polymer showed semiconducting properties. Lee et al. reported that the poly(1,8-DAN) synthesized in acetonitrile has reasonable conductivity in its doped form [62]. The sensitivity of poly(1,8-DAN) to heavy metal ions such as Ag^+, Hg^{2+} and Cu^{2+} has been studied using electrochemical and spectroscopic methods [63–65]. More recently, a series of diaminonaphthalene derivatives have been reported [66] and their optical and electrochemical behavior were investigated. These compounds could be used as optical probes in chemical sensors, biosensors and solar photovoltaic devices. PDAN fine particles have been also synthesized successfully by a simple chemical oxidation polymerization of DAN with $(NH_4)_2S_2O_8$ or $FeCl_3$ as oxidant with a high yield and productivity [67]. The structure and properties of the PDAN obtained depend strongly on the oxidant used. $FeCl_3$ oxidant will produce a ladder PDAN chain with less free $-NH_2$ groups, while $(NH_4)_2S_2O_8$ oxidant will produce a linear PDAN chain with much more free $-NH_2$ groups. Therefore, the polymer obtained using $(NH_4)_2S_2O_8$ exhibit high adsorbability by complexation between Ag^+ and amine/imine groups as well as the redox adsorption between Ag^+ and free $-NH_2$ group. Chemical in situ deposition of poly(1,8-diaminonaphthalene) on conductive supports in aqueous and acetonitrile solutions was also investigated using electrochemical quartz crystal microbalance (EQCM)