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Carbon nanotube composite coated platinum electrode for detection of Cr(III) in real samples

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Abstract

This paper demonstrates the application of composite multi-walled carbon nanotube (MWNT) polyvinylchloride (MWNT-PVC) based on 1,5-diphenylcarbazide as chromium ionophore in potentiometric measurement. The sensor shows a good Nernstian slope of 19.52 ± 0.40 mV/decade in a wide linear range concentration of 6.3×10^{-8} to 1.0×10^{-2} M for $Cr(NO_3)_3$. The detection limit of this electrode was found to be 3.2×10^{-8} M of $Cr(NO_3)_3$ and is applicable in a pH range of 3.0–6.8. It has a short response time of about 10 s. This chromium electrode has a good selectivity over 16 various metal ions. The practical analytical utility of this electrode was demonstrated by measurement of Cr(III) in drinking water and mineral water samples without any serious preliminary pre-treatment and chromium in multivitamin.

Keywords: Multi-walled carbon nanotube (MWNT); PVC; Carbon composite coated platinum electrode; Cr(III); 1,5-Diphenylcarbazide; Natural waters; Multivitamin

1. Introduction

Carbon nanofibers and nanotubes are promising to revolutionize several fields in material science and are a major component of nanotechnology [1].

Carbon electrodes are widely used in electroanalysis because of their low background current, wide potential window, chemical inertness, low cost and suitability for various sensing and detections. Several forms of carbon that are suitable for electroanalytical applications are available. The recent discovery of carbon nanotubes (CNTs), has attracted much attention because of their dimensions and structure sensitive properties [2]. The nanotubes consisted of up to several tens of graphitic shells (so called multi-walled carbon nanotubes, MWNT) with adjacent shell separation of ∼0.34 nm, diameters of ∼1 nm and high length/diameter ratio. Carbon nanotubes have a novel structure, a narrow distribution size, highly accessible surface area, low resistance, and high stability. It has been shown experimentally that the introduction of CNTs into a polymer matrix improves the electric conductivity as well as the mechanical properties of the original polymer matrix [1,3–5]. As for the electrical properties of CNT/polymer composites, it was reported that use of CNTs as conductive filters in a polymer matrix implies a very low percolation threshold [6]. However, as CNTs are generally insoluble in common solvents and polymers they tend to aggregate and disperse poorly in polymeric matrix, resulting in deleterious effects. To overcome these difficulties, several methods have been developed to disperse CNTs in host polymers. For example, CNTs could be dispersed in certain polymer solutions via ultrasonication [7,8].

Depending on chiral symmetry, CNTs conductivity may vary from metallic to semiconducting. The subtle electronic properties suggest that CNTs will have ability to mediate electron transfer reactions with an electroactive species in solution when used as an electrode. Multi-walled carbon nanotubes (MWNTs) were first used to construct the electrode and to probe bioelectrochemical reactions [9]. Though MWNTs have been used to response biomolecules, the electrochemical properties of MWNTs are less studies so far [10].

Over recent years, the electrodes and detectors those which are of specific interest are composites of insulating organic polymers filled with electrical conductors: carbon powders, ligand and additives [11,12]. Various forms of carbon or graphite with different polymers as binders were reported, glassy carbon electrodes [13–15], carbon film electrode [16] and carbon–polyvinylchloride are used for analytical detections [17–19]. Although conductor–polymer composites are being

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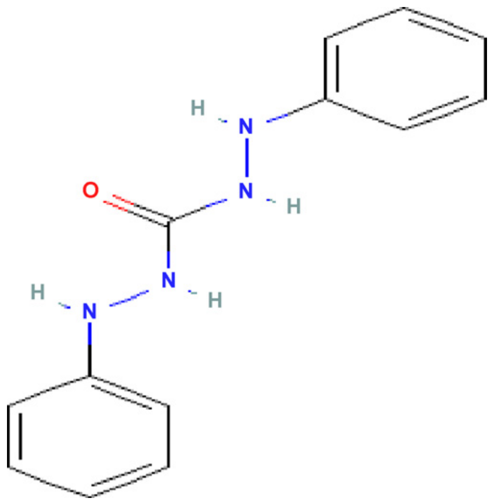

Fig. 1. 1,5-Diphenylcarbazide structure.

increasingly used in electrochemistry, carbon–polyvinylchloride composites are rarely used, due to difficulties in electrode preparation [20]. We demonstrated that the carbon–polyvinylchloride composite electrodes can be prepared easily on coated platinum wire electrode. Since the documented discovery of carbon nanotubes (CNT) by Iijima [21] and the realization of their unique physical properties, including mechanical, thermal, and electrical, many investigators have endeavoured to fabricate advanced CNT composite materials that exhibit one or more of these properties. For example, as conductive filler in polymers, CNT are quite effective compared to traditional carbon black micro particles, primarily due to their high aspect ratios [22,1].

Chromium may exist in environmental waters as Cr(III) and Cr(VI), the latter being the toxic and carcinogenic form. Since atomic absorption spectrometry (AAS) and inductively coupled plasma atomic emission spectrometry can only yield information on total Cr concentration [23]. Determination of chromium has received considerable attention because of highly toxic nature of Cr^{6+} and the useful biological activity of Cr^{3+} [24–26]. Chromium is one of the essential trace elements in multivitamin with multimineral pharmaceutical formulations that contain only Cr^{3+} either in the form of chromium chloride (inorganic source) or organic source [27], so it is important the detection of chromium(III) that exist in many biological and industry materials. In spite of, a lot of sensors for determination of trivalent metal ions have been reported [23], but only a few number of them is about chromium in potentiometric method [28–30].

1,5-Diphenylcarbazide (Fig. 1) used as an indicator in titrating iron and for the colorimetric determination of chromium. In this sensor 1,5-diphenylcarbazide was applied for Cr(III) detection. In literature it is reported that diphenylcarbazide (DPC) gives very sensitive color reaction with Cr(VI) in mineral acid medium and Cr(III)–diphenylcarbazone ($Cr(HL)_2^+$) complex occurs [31–33].

The first report on CWEs was published by Cattrall and Freiser [34] and then various CWEs were published [35]. Previously for the first time we reported the PVC (polyvinylchloride) carbon composite on platinum wire (CWE) for Ag(I), which in comparison to the most commercially available electrodes this electrode was readily prepared and exhibited a high selectivity and a low detection limit [36]. The significant of this membrane composition were in two parts, one is using of carbon powder for increasing sensitivity, and second part is application of bentonite which is an important factor for increasing selectivity of this composition. Research aimed at producing new nanocomposites with improved properties has drastically increased, especially on materials tailored at a nanometre level, such as carbon nanotubes. In an attempt to increase the sensitivity in the present work we applied composite electrode sensor based on MWNT.

This new composite that coating on platinum wire is a good sensitive and selective electrode. A wide concentration range (6.8×10^{-8} to 1.0×10^{-2} M) and detection limit was (3.2×10^{-8} M) obtained. This work suggests that MWNT have some specific properties compared to graphite powder and the development of this kind of carbon in PVC-composite is necessary. This new design is a simple, accurate, sensitive, inexpensive and relatively rapid method is applied for detection of Cr(III) in natural water.

2. Experimental

2.1. Reagents

All solutions were prepared from analytical reagents grade. Dibutylphthalate (DBP), dimethyl sebacate (DMS), diethyl sebacate (DES) and *o*-nitrophenyloctylether (*o*-NPOE) were obtained from Fluka; polyvinylchloride (PVC), multi-walled carbon nanotubes, and tetrahydrofuran (THF) were purchased from Merck; 1,5-diphenylcarbazide (Fig. 1) as ionophore was purchased from Fluka.

2.2. Electrode preparation

The schematic setup and general protocol for preparation of this sensing electrode used in this work was similar to our previous studies [29,37–40] except that this electrode was a MWNT composite PVC coated wire electrode with a chromium selective ionophore. This cocktail mixture was prepared by weighing ionophore (11.7%); MWNT (3.8%); DBP (56.4%); PVC (28.2%). A total weight of the mixture 220 mg dissolve in 1.5 cm^3 of dry freshly distilled THF. The mix for 20 min was in ultrasonic and the coating process of this carbon composite coated platinum wire electrode was performed by dipping Pt wire five times into this mixture. After each coating the membrane was air-dried for 12 h until a thin film was formed by using the technique as our previous work [37]. The electrode was finally conditioned for 60 min in a10^{-3} M of $Cr(NO_3)_3$ solution.

2.3. Apparatus and emf measurements

All measurements of emf were made at 25 °C using a Metrohm pH meter (Model 624) with a saturated calomel