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Enhanced sensitivity for Cu(II) by a salicylidine-functionalized polysiloxane carbon paste electrode

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ABSTRACT

A new approach for decreasing the detection limit for a copper(II) ion-selective electrode (ISE) is presented. The ISE is designed using salicylidine-functionalized polysiloxane in carbon paste. This work describes the attempts to develop the electrode and measurements of its characteristics. The new type of renewable three-dimensional chemically modified electrode could be used in a pH range of 2.3–5.4, and its detection limit is 2.7×10^{-8} mol L^{-1} (1.2 μg L^{-1}). This sensor exhibits a good Nernstian slope of 29.4 ± 0.5 mV/decade in a wide linear concentration range of 2.3×10^{-7} to 1.0×10^{-3} mol L^{-1} of Cu(II). It has a short response time (~8 s) and noticeably high selectivity over other Cu(II) selective electrodes. Finally, it was satisfactorily used as an indicator electrode in complexometric titration with EDTA and determination of copper(II) in miscellaneous samples such as urine and various water samples.

1. Introduction

Solid electrodes based on carbon materials are commonly used in electroanalysis due to their broad potential window, low background current, rich surface chemistry, low cost, chemical inertness and suitability for various sensing and detection applications [1,2]. Among them, carbon paste electrodes (CPEs) combine a carbon powder with a pasting liquid (an organic binder). The advantages of carbon paste electrodes drew the attention of researchers in recent years where these advantages were exploited for various measurements including potentiometric [3–7]. However the exact behaviour of carbon paste electrodes is not fully understood.

Silica-based organic–inorganic hybrids, most often dispersed in carbon paste electrodes, have been used for determination of metal ions [8].

Chemical modification of electrode surfaces is a strategy for improving the analytical performance of conventional electrode materials for specific applications in various fields, especially electroanalysis and sensors [9].

Silica-based organic–inorganic hybrids combine in a single solid both the properties of a rigid three-dimensional silica network with particular reactivity of the organic components [9,10]. These multifunctional materials are robust inorganic solids displaying both high specific surface area and open surfaces interconnected to each other. They have been reported to be particularly suitable to design integrated electrochemical systems that likely offer attractive features in the field of electroanalytical chemistry [11,12]. These materials can be manufactured quite easily at room temperature by the sol–gel process and the resultant material will have properties of the tailor-based materials incorporated in the polymer. Therefore, these polymers were applied in various fields including chemical and biological sensors, separation processes and catalysis [13–17]. In particular, it is noted that organic and inorganic components are usually linked through strong chemical bonds and can coordinate metal ions efficiently. The complex-impregnated polymer has properties that can be utilized for specific targets. Use of silica gel in a sensor is likely to improve the detection limit because of its strong polar bonds, between silicon and oxygen, that can improve conductivity of the electrode and enhance its response.

Potentiometric determination of copper using carbon paste electrodes assumes importance in view of its widespread occurrence in various samples [3,18–20]. Copper deficiency results in anemia while its accumulation results in Wilson disease (WD) [21]. Therefore, devising proper methods for its determination in various samples is of utmost importance. In this work, a silica gel surface chemically modified with salicylaldehyde was prepared, characterized and found as a sensing material for Cu(II); it was employed in construction of an electrode that has competitive properties over many other electrodes.

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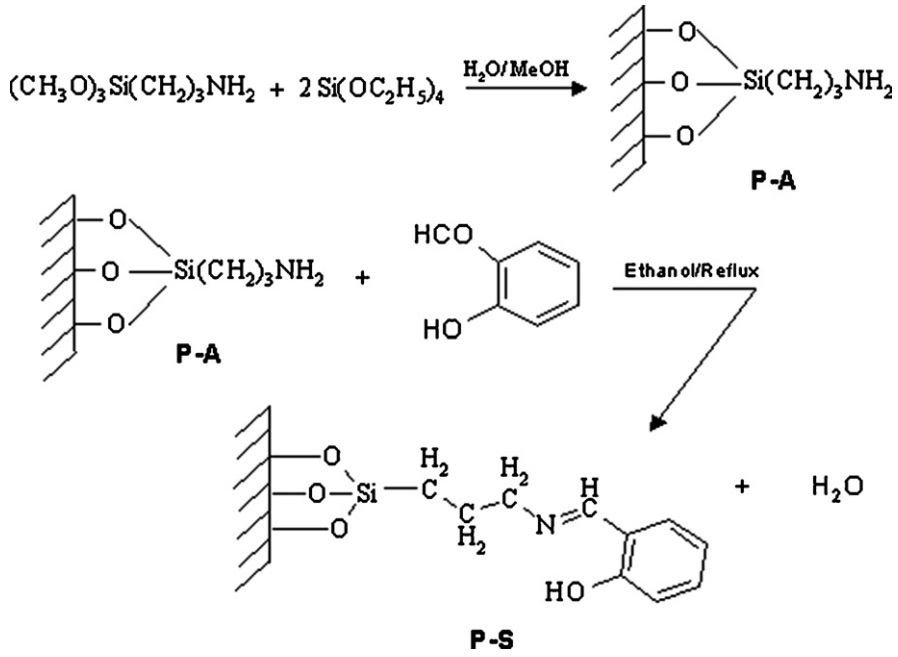

Scheme 1. Preparation of 3-aminopropylpolysiloxane (P–A) and salicylic dinepropylimine polysiloxane ligand system (P–S).

2. Experimental

2.1. Reagents and materials

All chemicals used were of analytical grade. Tetraethylorthosilicate, 3-aminopropyltrimethoxysilane, and salicylaldehyde were purchased from Merk. Salicylaldehyde was obtained from Riedel-de Haen. Reagent grade pure graphite powder, bis(2-ethylhexyl) adipate (DOA), dioctyl phthalate (DOP), dibutyl phthalate (DBP), tris(2-ethylhexyl) phosphate (DOPh), dioctyl sebacate (DOS), paraffin oils (P.O.), as well as all metal salts such as chlorides, nitrates and sulphates were purchased from Aldrich. Diethyl ether and methanol (pectroscopic grade) were commercially available. All reagents and solvents were used as received.

2.2. Apparatus

All EMF measurements were carried out with the following assembly:

Hg, Hg_2Cl_2(s), KCl(sat.) || sample solution | carbon paste electrode.

The potential measurements were carried out at 25 ± 0.1 with a digital millivoltmeter (SR-MUL-3800). pH measurements were made on a digital pH meter (HANNA pH 211). A saturated calomel electrode (SCE) was used as a reference electrode. Analysis for carbon, hydrogen, and nitrogen were carried out, using an Elemental Analyzer EA 1110-CHNS CE Instrument. The infrared spectra for the materials were recorded on a PerkinElmer FTIR spectrophotometer using KBr disk in the range 4000–400 cm^{-1}.

2.3. Preparations

2.3.1. Preparation of modified carbon paste electrode

A modified carbon paste electrode was prepared according to a previously reported method [22]. The paste was prepared by thoroughly mixing weighed amounts of the ionophore, high purity graphite and plasticizers as shown in Table 2 in plastic Petri dishes until a uniformly wet paste was obtained which was used for sensor construction. Electrode bodies were made from 1 mL polypropylene syringes (3 mm i.d.), the tip of which had been cut off with a cutter. The mixture was packed in the end of the syringe. Electrical contact to the carbon paste was made by a copper wire. A fresh electrode surface was obtained by squeezing out a small amount of paste and scraping off the excess against a conventional paper then polishing the electrode on a smooth paper to obtain a shiny appearance. The electrode was used directly for potentiometric measurements without pre-conditioning.

2.3.2. Synthesis of 3-aminopropylpolysiloxane (P–A)

Aminopropylpolysiloxane was prepared by adding 3-aminopropyltrimethoxysilane (9.86 g, 50 mmol) to a stirred solution of tetraethylorthosilicate (20.83 g, 100 mmol) in 15 mL methanol and HCl (9.95 mL, 0.42 mol L^{-1}). Gelation occurred within a few seconds. The product was left to stand for 12 h then dried in a vacuum oven at 90 °C. The material was crushed, sieved, washed successively with 50 mL portions of 0.025 mol L^{-1} NaOH, water, methanol and diethyl ether and then dried in vacuum oven at 90 °C at 0.1 torr for 10 h. The elemental analysis for the aminopropylpolysiloxane is given in Table 1.

2.3.3. Synthesis of salicylidinepropylimine polysiloxane ligand system (P–S)

3-Aminopropylpolysiloxane (P–A) (5.0 g, 17.5 mmol) was refluxed for 12 h with an excess (5 g, 41 mmol) of salicylaldehyde in 50 mL ethanol. The solid product was filtered off, washed successively with 50 mL portions of 0.025 mol L^{-1} NaOH, methanol

Table 1
Elemental analysis data for P–A and P–G

Polysiloxane	%C	%H	%N	C/N
P–A				
Expected	15.7	3.9	6.1	3.0
Found	13.1	4.6	4.9	3.1
P–S				
Expected	30.9	3.1	3.6	10.0
Found	24.68	3.8	4.3	6.69