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Potentiometric detection of silver (I) ion based on carbon paste electrode modified with diazo-thiophenol-functionalized nanoporous silica gel

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ABSTRACT

For the first time, triazene compound functionalized silica gel was incorporated into carbon paste electrode for the potentiometric detection of silver (I) ion. A novel diazo-thiophenol-functionalized silica gel (DTPSG) was synthesized, and the presence of DTPSG acted as not only a paste binder, but also a reactive material. The electrode with optimum composition, exhibited an excellent Nernstian response to Ag^+ ion ranging from 1.0×10^{-6} to 1.0×10^{-1} M with a detection limit of 9.5×10^{-7} M and a slope of 60.4 ± 0.2 mV dec^{-1} over a wide pH range (4.0–9.0) with a fast response time (50 s) at 25 °C. The electrode also showed a long-time stability, high selectivity and reproducibility. The response mechanism of the proposed electrode was investigated by using AC impedance. Moreover, the electrode was successfully applied for the determination of silver ions in radiology films, and for potentiometric titration of the mixture solution of Cl^- and Br^- ions.

1. Introduction

Nowadays silver appears in a wide range of products such as electronic products, alloys, jewelry and photographic material. On account of their antibacterial properties, silver and its compounds have been widely used today in the medical and health care fields. Consequently, large amounts of silver are released into the environment annually. It is reported that the concentration of silver in water higher than 1.6 nM is toxic to fish and microorganisms. It has also been found that silver is toxic to humans at a concentration as high as 0.9 μM in drinking water [1–5]. With due attention to the above, determination of silver (I) in samples is necessary.

In the past five decades, a number of silver selective electrodes have been developed based on different ionophores including Schiff base [6], crown ethers [7–9] and benzothiazole calix[4]arene [10]. However, complicated and tedious synthesis of the above ionophores limits the analytical applications of the sensors. In addition, the plasticizer, carrier or ionic site leaching from the polymeric film into solution results in the limited lifetime of the above PVC membrane electrodes. In principle, this shift reduces the selectivity and deteriorates the response of electrodes [11].

To date, the silica-based organic–inorganic hybrids have become attractive electrode modifiers. On the one hand, they are robust inorganic solids with the properties of a rigid three-dimensional structure. On the other hand, they possess the particular chemical reactivity of organic component. The electrode modifier, able to preconcentrate metallic ions on the electrode surface either by complexation or electrostatic attraction, can lead to more sensitive electroanalytical procedures with lower detection limit values [12–14]. Carbon paste electrode (CPE) is one of the convenient conductive matrixes to prepare the chemically modified electrodes (CMEs), because a selective agent is incorporated into the surface by simple mixing with graphite powder and paraffin oil [15]. Thus, carbon paste electrode has aroused attention due to its advantages such as easy construction and regeneration, stable electrochemical response and lower ohmic resistance [16,17].

In recent years, carbon paste electrodes based on functionalized nanoporous silica gels have been used for detection of Ag [14,15], Cu [12,18], Hg [19,20] and Cd [21]. To the best of our knowledge, this work is the first attempt to apply triazene compound functionalized silica gel for the determination of silver ion. Triazene compounds possessing a diazoamino group (–N=N–N–) have been studied for over 130 years due to their interesting structural, anticancer and reactivity properties. However, in spite of extensive reports on the synthesis, characterization and crystalline structure of the transition metal triazenide complexes, reports on analytical application of these ligands are quite spare [22–24]. The functionalized nanoporous silica gels with diazo-thiophenol groups were covalently attached to the solid framework via N-(2-aminoethyl)-3-aminopropyl chains. According to the hard–soft acid base (HSAB) concept [25], the presence of aminothiophenol molecules, carrying soft S-donor atoms as part of a macrocyclic ligand, has a marked influence on the coordination of silver (I) as a soft Lewis acid. The diazo-thiophenol-functionalized silica gel (DTPSG), with group containing S,

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N and O atoms, is expected to provide a much-needed hydrophobic environment and high complex stability. Meanwhile, the possible cation-π interactions could have a marked influence on the coordination geometry at the metal center [10,12]. So, DTPSG is a very efficient material to improve the lifetime of the proposed modified carbon paste electrode. Finally the sensor properties were successfully evaluated by its application to the potentiometric titration of the mixture of chlorine, bromine ions and the determination of silver ions in radiology films.

2. Experimental

2.1. Reagents and apparatus

Silica gel 60 was purchased from Merch and activated by refluxing in hydrochloric acid (4 M) for 24 h before use. N-(2-aminoethyl)-3-aminopropyl-trimethoxy silane and 2-aminothiophenol were purchased from J&K Chemical Ltd. Graphite powder was purchased from Sigma. Reagent grade paraffin oil and the nitrate salts of the used cations were purchased from Chongqing Chemicals (Chongqing, China). All of the chemicals used were of analytical-regent grade. All aqueous solutions were prepared with deionized distilled water.

Potentiometric measurements were performed with a MP230 pH meter (Mettler Toledo, Switzerland) and a pHS-3C digital ion analyzer (Dazhong Analytical Instruments, Shanghai, China). IR spectra were recorded with a Spectrum GX FTIR instrument (Mattson RK-6000, USA). The AC impedance was recorded with an impedance measurement unit (IM6e, ZAHNER elektrick Co., Germany) and the frequency range used was 10^{-2}–10^{6} Hz (25 °C). A Model TAS-986 atomic absorption spectrophotometer (AAS) (Purkinje, Beijing, China) was used for the analysis of real samples.

2.2. Synthesis of diazo-thiophenol-functionalized silica gel (DTPSG)

A mixture of 10 g of activated silica gel with 30 mmol of N-(2-aminoethyl)-3-aminopropyl-trimethoxy silane was refluxed in toluene under nitrogen atmosphere for 24 h [18,20]. The attained solid, grafted amino silica gel (GANSG), was washed with warm toluene several times. For the preparation of the surface bound DTPSG ligand (Fig. 1), 2-aminothiophenol (0.63 g) was dissolved in 0.6 mL 37% hydrochloric acid and the solution was then cooled to 0–5 °C. Then, 2 mL of 20% $NaNO_2$ was added to the above mentioned mixture and the resulting solution was stirred for 1 h to give a bright yellow solution [26]. GANSG (0.6 g) was dispersed in the solution of Na_2CO_3 (1.8 g Na_2CO_3 + 15 mL H_2O). Then the solution of GANSG was added dropwise to the bright yellow solution. After stirring for 4 h, the reaction mixture was neutralized with HCl. The brown crude solid was filtered and then was washed with water three times. Last, the brown crude solid was recrystallized from ethanol to afford a pure product. IR characterization of DTPSG was measured by using KBr squash method. Solid DTPSG (2 mg) was used in 200 mg KBr to prepare KBr Tablet.

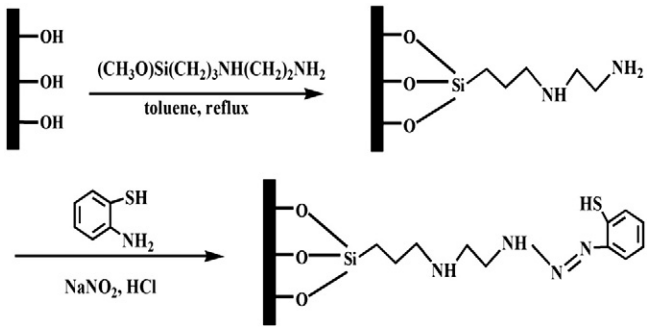

Fig. 1. Schematic representation of the synthetic procedure of DTPSG.

Then, IR spectra were recorded with a Spectrum GX FTIR instrument (Mattson RK-6000, USA). Infrared spectral data are as follows: (IR KBr): 3417 cm^{-1} (N–H), 3205 cm^{-1} (Ar–H), 2364 cm^{-1} (N–N═N), 1108 cm^{-1} (Si–O), and 784 cm^{-1} (Si–C).

2.3. Preparation of the chemically modified carbon paste electrodes

The chemically modified carbon paste electrodes were prepared by thoroughly hand-mixing graphite powder, paraffin oil and DTPSG. A disposable polyethylene syringe (3 mm i.d., 3 cm) was used as the electrode body. After the mixture homogenization, the paste was packed into the plastic tube tip to avoid possible air gaps, often enhancing the electrode resistance. A copper wire was inserted into the opposite end to establish electrical contact. The external electrode surface was polished on a soft paper. A new surface was produced by scraping out the old surface.

2.4. Electrode conditioning and EMF measurement

The electrodes were conditioned for 24 h in pH 4.0 HNO_3 solution. A digital ion analyzer Model pHS-3C was used for the potential measurements at ambient temperature. Saturated calomel electrode was used as the reference electrode. The electrochemical cell can be represented as follows:

$$Hg\text{–}Hg_2Cl_2, KC1(satd.)|\ 1.0\ M\ KNO_3|\ test\ solution\ ||\ carbon\ paste\ electrode\ ||\ Cu.$$

Activities were calculated according to the Debye–Hückel procedure [27].

3. Results and discussion

3.1. Electrode composition and response characteristics of the CPEs

In initial experiments, carbon paste electrodes containing diazo-thiophenol-functionalized silica gel (DTPSG) were used for the detection of different cations (Fig. 2). The electrode exhibited a good selectivity for Ag^{+} in comparison with other cations. It is possible that the presence of S, N and O atoms in DTPSG may generate a great affinity between the ionophore and the Ag^{+} ion. On the one hand, DTPSG containing soft S-donor atoms has a marked influence on the coordination of silver (I) as a soft Lewis acid [25]. On the other hand, DTPSG contains strong covalent bonds (diazo-thiophenol groups covalently attached to the solid framework via N-(2-aminoethyl)-3-aminopropyl chains), which are likely to provide a much-needed hydrophobic environment to stabilize the complexes formed by ions and ionophore [28,29].

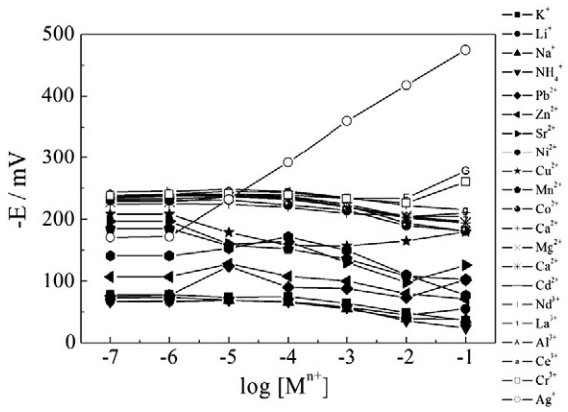

Fig. 2. Potential responses of carbon paste electrode based on DTPSG for various cations.