Talanta 84 (2011) 49–52

Contents lists available at ScienceDirect

Talanta

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

Application of cement as new electrode material and solid-phase microextraction material demonstrated by electrochemiluminescent detection of perphenazine

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ARTICLE INFO

Article history:
Received 10 September 2010
Received in revised form
25 November 2010
Accepted 4 December 2010
Available online 13 December 2010

Keywords:
Cement
Cement carbon electrode
Solid-phase microextraction
Electrochemiluminescence
Perphenazine

ABSTRACT

Because of its unique pore network, good strength, and low cost, cement was used as a new electrode material and solid-phase microextraction (SPME) material for the first time. It was mixed with carbon to make a new electrode, cement carbon electrode (CCE). The as-prepared CCE was used to demonstrate the application of cement in SPME by $Ru(bpy)_3^{2+}$ electrochemiluminescent detection of perphenazine (PPZ). The calibration plot for PPZ is linear from 1.0×10^{-9} to 3.0×10^{-6} M with a detection limit of 3.1×10^{-10} M. The method was successfully applied to the detection of PPZ in urine sample. Cement-based electrode material may also find broad applications in electrochemistry industry, such as electrochemical wastewater treatment.

1. Introduction

Solid-phase microextraction (SPME) preserves all the advantages of solid-phase extraction such as simplicity, low cost, easy automation, and on-site sampling and, at the same time, eliminates the disadvantages of solid-phase extraction such as plugging and the use of solvents [1,2]. As a result, it has become an important sample preparation technique for the analysis of organic compounds. Various materials have been used as solid support for SPME, such as inorganic oxides, chemically bonded silicas, porous polymers, metal-organic frameworks, immunosorbents, as well as the low cost materials of stainless steel wires, molecularly imprinted polymers and carbon [2–6].

Cement is widely used manufactured material and is free of organic compounds. When cement is mixed with water, it can automatically form porous material [7]. This porous cement-based material is promising for SPME of organic compounds. Since carbon is frequently used not only as a cheap SPME material but also as an electrode material, it was chosen as a representative to mix with cement to construct a new SPME material, cement carbon. The good conductivity of cement carbon allows preparing cement carbon electrode (CCE), and thus allows simultaneously demonstrating the applications of cement as electrode material and SPME material.

Tris(2,2′-bipyridyl)ruthenium (II) is a typical surface-insensitive redox system. Its electrochemiluminescence (ECL) is a powerful electrochemical technique for immunoassays, DNA probe assays, and the determination of organic compounds [8–23]. Perphenazine (PPZ), a popular antipsychotic drug, is roughly five times as potent as chlorpromazine and has less sedative and adrenolytic properties [24]. It has never been determined by ECL method. Therefore, the application of cement as a SPME material and electrode material was demonstrated by ECL determination of PPZ in this study.

2. Experimental

Tris(2,2′-bipyridyl)ruthenium(II) chloride (>99.95%) and PPZ were purchased from Aldrich and Sigma, respectively. Graphite powder (spectroscopically pure grade) was obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Cement was produced from Jilin Yatai (Group) Co., Ltd. (Changchun, China). All other reagents were of analytical grade. The urine sample was obtained from one healthy volunteer. Electrochemical measurements were performed in a conventional three-electrode cell with a CHI 800B potentiostat (CH Instruments, Shanghai Chenhua, China). The three-electrode system included a CCE (diameter 2 mm), an Ag/AgCl (saturated KCl) reference electrode, and a Pt wire auxiliary electrode.

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doi:10.1016/j.talanta.2010.12.009

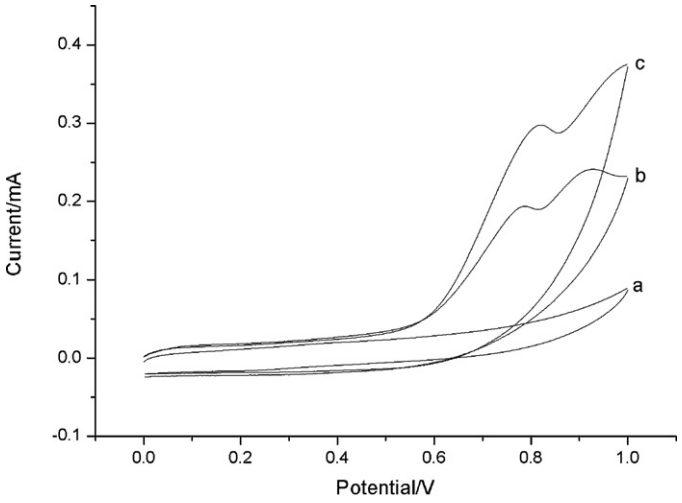

Fig. 1. Cyclic voltammograms of accumulated PPZ at a CCE in 0.05 M phosphate buffer solution (pH 8.0) after SPME in a stirred 0.05 M phosphate buffer solution (pH 8.0) containing 10 μM PPZ with increasing time: (a) 0, (b) 4, (c) 10 min, scan rate, 50 mV/s.

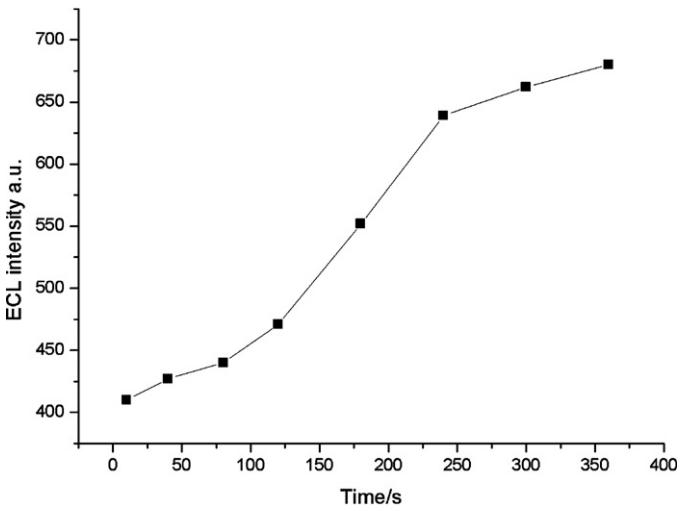

Fig. 2. ECL intensities as a function of accumulation time at the CCE in 0.05 M phosphate buffer solution (pH 8.0) containing 1 μM PPZ.

The CCE was fabricated by thoroughly hand-mixing appropriate amount of graphite powder, cement and deionized water in a mortar and pestle, followed by packing the resulting paste firmly into the electrode cavity of a Teflon sleeve and hardened at the room temperature. The diameter of the CCE is 2 mm, and the surface area for SPME is 3.14 mm^2. A fresh working electrode surface was obtained by polishing the prepared CCE on the abrasive paper. The CCE was first immersed in a stirred sample solution for SPME of PPZ, and was then moved to 1 mM $Ru(bpy)_3^{2+}$ solution for the ECL measurement with a BPCL Ultra-Weak luminescence analyzer, which was purchased from Institute of Biophysics, Chinese Academic of Sciences. Unless noted otherwise, the PMT was biased at 800 V. To measure the concentration of PPZ in urine samples, urine samples were diluted (1:4) with the supporting electrolyte after storage at room temperature for 5 h, spiked with PPZ, and measured. The morphology of CCMs was inspected using a scanning electron microscope (FE-SEM, Hitachi S-4800), and the morphology of cement was carried out on a PHILIPS XL-30 ESEM.

3. Results and discussion

3.1. Electrochemistry of PPZ following SPME

The SPME process at the CCE is a combination of extraction at carbon powder and penetration into the interior CCE. Fig. 1 shows cyclic voltammograms of accumulated PPZ with different SPME time. Accumulated PPZ at the CCE exhibits an irreversible oxidation behavior in 0.05 M pH 7.0 phosphate buffer solution, because its oxidation products undergo very rapid nucleophilic attack to yield adducts which are not reducible at potentials in the vicinity of their oxidation wave [25]. The oxidation peak increases with increasing accumulation time, indicating that CCE is an effective material for the SPME of PPZ.

3.2. Optimization of experimental conditions for the ECL reaction of $Ru(bpy)_3^{2+}$/PPZ

The effect of potential on the ECL intensity was examined over a range of 0.9–1.4 V. The ECL intensity increases rapidly as the potential shifts positively and reaches the vertex at 1.35 V. To get good reproducibility and sensitivity, subsequent experiments were conducted at a potential of 1.35 V for ECL excitation. The dependence of ECL intensity on pH was also studied. The ECL signals obtained at the CCE constantly increases with increasing pH from 4 to 7 and then decreases slightly at pH higher than 8. This phenomenon is similar to that in the $Ru(bpy)_3^{2+}$/tripropylamine system. The intense pH dependence of the $Ru(bpy)_3^{2+}$/PPZ ECL reaction may mainly result from pH dependence of deprotonation of PPZ and its radical cation, and the consumption of the electrogenerated $Ru(bpy)_3^{3+}$ by water at high pH values [26].

3.3. Optimization of experimental conditions for SPME of PPZ

Fig. 2 shows the influence of extraction time on the ECL intensities. The ECL intensities increase rapidly with accumulation time and level off at 4 min. The enhanced intensities at longer time are ascribed to the accumulation of more PPZ. It is faster than the extraction at other carbon paste electrodes [27]. Fig. 3A exhibits a typical SEM image of the as-prepared CCE and Fig. 3B shows the SEM image of cement prepared in the same way. After cement was mixed with graphite, abundant graphite layer structure emerged and CCE is still porous. It seems that the porosity of CCE and hydrophilicity of cement facilitate the SPME of PPZ to carbon in aqueous solutions.

Fig. 4 shows the effect of pH of PPZ solutions on the ECL intensity. The ECL intensity increases rapidly as the solution pH changes from 6 to 8 and levels off at pH higher than 8. The results are attributed to the increase in the concentration of the neutral form of PPZ with increasing pH of PPZ solutions, which results in a higher affinity of PPZ toward CCE. Therefore, a pH of 8.0 was used for the further measurements.

The influence of cement content on the ECL intensity was also investigated by varying the weight ratio of graphite powder to cement at 5:1, 5:2, 5:3, 5:4, and 1:1. When the content of cement in CCE is too low (5:1), it is difficult to form solid CCEs while the content of cement in CCE is too high (higher than 1:1), the resistances of CCEs increase. Fig. 5 shows the dependence of the ECL intensity on the content of cement when 1 μM PPZ was detected. The maximum ECL intensity is obtained at a ratio of 5:3. Under optimum conditions, the relative standard deviation is 3.7% for the quantification of 1 μM PPZ at seven electrodes with the ratio of 5:3.

3.4. Calibration curve

The ECL intensities vary linearly with log of PPZ concentration over the range of 1.0×10^{-9}–3.0×10^{-6} M under optimum con-

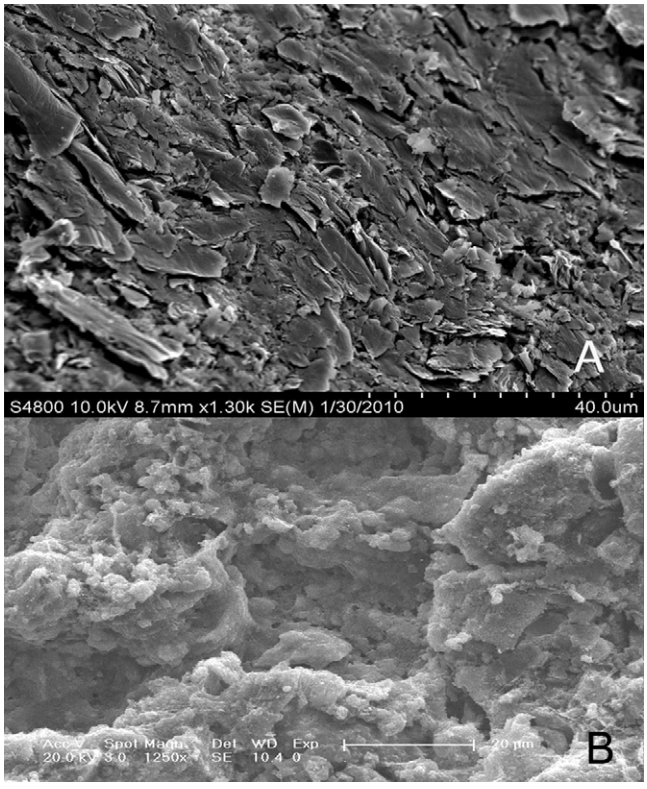

Fig. 3. SEM images of (A) CCE and (B) cement.

ditions (slope = 1.3×10^2; intercept = 1.29×10^3; $n = 8$; correlation coefficient = 0.999). The detection limit is 3.1×10^{-10} M at a signal-to-noise ratio of 3. The relative standard deviation (RSD) is 3.6% for six replicate measurements of 0.3 μM PPZ. The total analysis time was less than 8 min.

3.5. Interference study and sample analysis

A number of substances commonly found in urine can react with tris(2,2′-bipyridine)ruthenium(II) to yield ECL. Fig. 6 shows the influence of these potential interferents to the detection of PPZ. Solutions of 0.5 mM ascorbic acid (AA), threonine (Thr), glutamic acid (Glu), and tyrosine (Tyr), 1 mM alanine (Ala), serine (Ser) and oxalate (Oxa), as well as 2 mM glycine (Gly), lysine (Lys), and histidine (His) do not interfere with the determination of 1 μM PPZ. The investigated concentrations of the interferents are higher than their concentrations in normal urine samples, respectively [28]. The tolerable limit of a foreign species was taken as a relative error less than 5%. The selectivity observed is likely due to the following reasons. First, the medium-exchange approach (a transfer of the working electrode from the sample solution to $Ru(bpy)_3^{2+}$ solution) was adopted in the present method [29,30], so interferences from species that cannot be accumulated onto the CCE have been minimized. Second, ECL efficiencies of the interfering species investigated are less than that of PPZ, a tertiary amine [31].

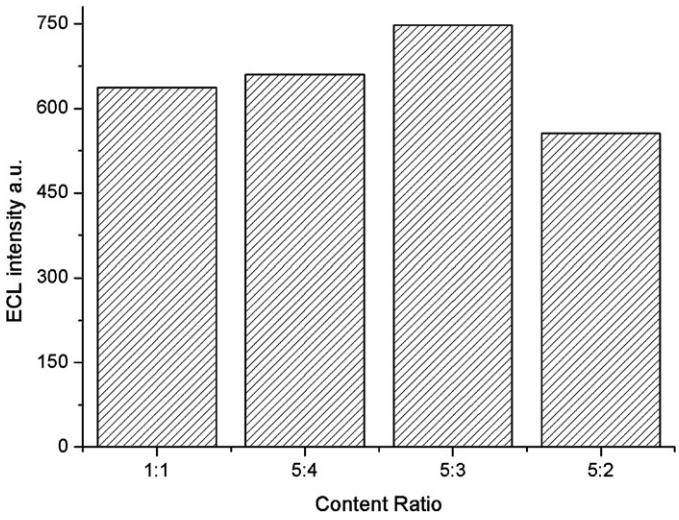

Fig. 5. Influence of cement content on the ECL intensities at CCE following 4-min extraction in 1 μM PPZ solutions.

The concentration dependence and precision studies were performed utilizing urine samples after storage at room temperature for 5 h. Prior to use, the urine samples were diluted (1:4) with the supporting electrolyte and then the PPZ solution was prepared with the diluted urine sample. A linear calibration is obtained over the range of 3×10^{-9}–3×10^{-6} M (slope = 81.8; intercept = 1.25×10^3; correlation coefficient = 0.989; $n = 7$) with a detection limit of 1.6×10^{-9} M. The relative standard deviation of six repeated detections of 1 μM PPZ is 4.1%. The analytical recovery and RSD of the

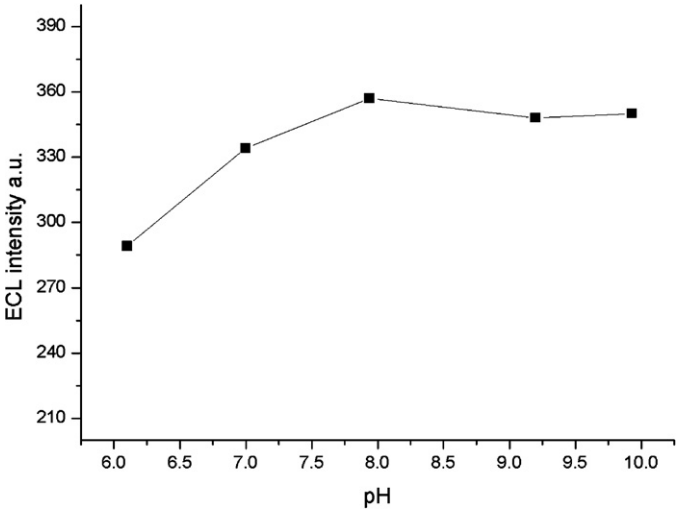

Fig. 4. Effect of pH of 1 μM PPZ solutions on the ECL intensities at CCE following 4-min extraction.

Fig. 6. Comparison of ECL intensity of 1 μM PPZ and ECL intensity of 1 μM PPZ with the addition of 0.5 mM AA, 0.5 mM Thr, 0.5 mM Glu, 0.5 mM Tyr, 1 mM Ala, 1 mM Ser, 1 mM Oxa, 2 mM His, 2 mM Gly, or 2 mM Lys. Error bars show the relative standard deviation of three replicate determinations.

supplemented 3×10^{-8} M PPZ were 101.8% and 3.8% ($n = 3$), respectively.

4. Conclusions

The applications of cement have been extended to SPME and electrochemistry. The porosity of cement carbon, the hydrophobicity of carbon, as well as the strong binding capacity and hydrophilicity of cement renders cement carbon an excellent SPME material for organic compounds. The nice conductivity, good stability, and easy renewal make cement carbon an attractive electrode material. Because both cement and carbon are very cheap, cement carbon is a promising disposal SPME and/or electrode material. Since cement can bind lots of materials, such as carbon nanotube, graphene, carbon fiber, carbon nanofiber, metal nanoparticle, and semiconductor nanocrystals, cement-based composites will find wide applications [32–34]. For example, cement-based electrode materials may find applications in electrochemical industry, such as electrochemical wastewater treatment.

Acknowledgements

This project was supported by the National Natural Science Foundation of China (Nos. 20505016 and 20875086), the Ministry of Science and Technology of the People's Republic of China (No. 2006BAE03B08), and the Department of Sciences & Technology of Jilin Province (Nos. 20070108 and 20082104).

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