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Stripping voltammetric detection of mercury(II) based on a surface ion imprinting strategy in electropolymerized microporous poly(2-mercaptobenzothiazole) films modified glassy carbon electrode

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ABSTRACT

This work reports a surface ion imprinting strategy in electropolymerized microporous poly(2-mercaptobenzothiazole) (MPMBT) films at the surface of glassy carbon electrode (GCE) for the electrochemical detection of Hg(II). The Hg(II)-imprinted MPMBT/GCE exhibits larger binding to functionalized capacity, faster binding kinetics and higher selectivity to template Hg(II) due to their high ratio of surface-imprinted sites, larger surface-to-volume ratios, the complete removal of Hg(II) templates and larger affinity to Hg(II). The square wave anodic stripping voltammetry (SW ASV) response of the Hg(II)-imprinted MPMBT/GCE to Hg(II) is ca. 3.0 and 5.9 times larger than that at the direct imprinted poly(2-mercaptobenzothiazole) modified GCE and non-imprinted MPMBT/GCE sensor, respectively; and the detection limit for Hg(II) is 0.1 nM (which is well below the guideline value given by the World Health Organization). Excellent wide linear range (1.0–160.0 nM) and good repeatability (relative standard deviation of 2.5%) were obtained for Hg(II). The interference experiments showed that mercury signal was not interfered in the presence of Pb(II), Cd(II), Zn(II), Cu(II) and Ag(I), respectively. These values, particularly the high sensitivity and excellent selectivity compared favorably with previously reported methods in the area of electrochemical Hg(II) detection, demonstrate the feasibility of using the prepared Hg(II)-imprinted MPMBT/GCE for efficient determination of Hg(II) in aqueous environmental samples.

1. Introduction

Mercury is one of the most well known toxic metals and has been considered as a human health hazard because it may cause serious health problems like kidney and respiratory failure, damage in the gastrointestinal tract and nervous system, and impairment of speech, hearing, and working [1]. Due to its high toxicity and accumulative character, rapid and reliable determination of trace Hg(II) has become increasingly desirable. Compared to other techniques [2–5], electrochemical technique for Hg(II) determination has received particular attention due to the inherent advantages such as high sensitivity and selectivity, impressive cost-effectivity and miniaturization, and so on. Pursue of a new electrochemical sensing interface is always one of the most important goals in this area. Quite a few different pathways for the voltammetric determination of Hg(II) have been developed including p-tert-butylthiacalix[4]arene modified glassy carbon electrode (GCE) [6], 2,5-dimercapto-1,3,4-thiadiazole modified GCE [7], poly(2-mercaptobenzothiazole) film modified GCE [8], polyviologen modified GCE [9], poly(EDTA-like) film modified carbon electrode [10], poly(3-methylthiophene) modified carbon electrode [11], oligonucleotides modified gold electrode, [12,13] 2-mercaptobenzimidazole modified gold electrode [14], gold nanoelectrode ensembles [15] and poly(vinylferrocenium) modified Pt electrode [16], etc. At these modified electrodes, the specificity of particular ligands toward target Hg(II) always results from a conventional acid–base complexation interaction between the ligands and Hg(II). Although some of these particular ligands can exhibit specific interactions with Hg(II), the other soft Lewis acids (such as Cd(II), Zn(II), Cu(II), and Ag(I)) also can exhibit specific interactions with the ligands. The selectivity of these ligands is usually unremarkable because many other metal ions have the ability to bind with the particular ligands without consideration of the stereochemical interactions between the ligands and metal ions.

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Recently, a biomimetic ion imprinted technique (that is, using metal ion as template) has become a potential tool for the preparation of robust materials that have the ability to specifically bind a metal ion species with high selectivity [17–23]. However, most of these traditional imprinting techniques suffer from low binding capacity, poor site accessibility, and slow binding kinetics because of most imprinted sites were embedded in high rigid polymer matrix interior [24,25]. It is well known that the sensitivity of the imprinted sensor is dictated by the amount of effective imprinted sites on the sensor surface. Therefore, controlling template ions to locate at the surface or in the proximity of materials' surface is critical to create more effective imprinted sites and to improve sites accessibility [26]. To achieve surface ion imprinting, the simplest method is imprinting ions at the various core surfaces to obtain the core–shell imprinted particles. Of various core materials, SiO_2 particles are ideal materials for surface imprinting various inorganic, organic or biological molecules, because of mechanical/chemical stability, low cost, easy preparation and the ability to functionalize [27]. Furthermore, SiO_2 particles can be easily etched by aqueous HF to form surface imprinted macroporous materials [28]. The surface imprinted macroporous materials were expected to provide a high ratio of imprinted sites and to enhance the total amount of effective imprinted sites to template ion, and can also offer increased mass transport and easier accessibility to the active sites through the material.

In this work, we report a surface ion imprinting strategy in electropolymerized microporous poly(2-mercaptobenzothiazole) (MPMBT) films at the surface of GCE for the electrochemical detection of Hg(II). The Hg(II)-imprinted MPMBT films modified GCE exhibit the larger binding to functionalized capacity, faster binding kinetics and higher selectivity to template Hg(II) due to their higher ratio of surface-imprinted sites, larger surface-to-volume ratios, the complete removal of Hg(II) templates and larger affinity to Hg(II) templates. The ion imprinted polymers (IIP)-based electrochemical sensor not only can strikingly improve the sensitivity and selectivity for Hg(II) analysis, but also obtains good repeatability and, thus, can be potentially exploited for on-line enrichment and detection of Hg(II) in environment.

2. Experimental

2.1. Reagents

Tetraethylorthosilicate (TEOS), 3-chloropropyltriethoxysilane (CPTS) 95% (M = 240.81), 2-mercaptobenzothiazole (MBT) 98% (M = 167.25) and Hg(II) nitrate were purchased from Sigma–Aldrich and used as supplied. Organic solvents (toluene, dimethylformamide (DMF), diethyl ether and ethanol) were supplied by Shanghai Chemicals Ltd. All other reagents were commercially available as analytical reagent grade. Stock solutions of Hg(II) were prepared by dissolving Hg(II) nitrate monohydrate 98% (Sigma–Aldrich) in the minimum required amount of nitric acid and were then appropriately diluted prior to experiments.

2.2. Apparatus

Electrochemical measurements were performed using an electrochemical analyzer LK2005A (Tianjin, China) connected to a personal computer. A three-electrode configuration was employed, consisting of a bare or modified glassy carbon electrode (GCE, 2 mm in diameter) as a working electrode and an Ag/AgCl/saturated KCl electrode and a platinum wire (1 mm in diameter) as the reference electrode and auxiliary electrode, respectively. The morphology of the MPMBT films was verified by field-emission scanning electron microscopy (FESEM, JEOL JSM-6700F, 10 kV).

2.3. Synthesis and chemical modification of SiO_2 particles

Uniform SiO_2 particles (~310 nm) were synthesized by hydrolysis of TEOS with aqueous ammonia, according to the reported Stöber method [29]. Subsequently, the SiO_2 particles were chemically modified with MBT to obtain the MBT-capping SiO_2 particles [30]. Typically, 0.1 g of SiO_2 particles was suspended in 20 mL of dry toluene and 1.75 mL (7.26 mM) of CPTS were added. The mixture was stirred for 48 h under reflux conditions in a nitrogen atmosphere. The resulting product (Cl–SiO_2) was filtered off and washed with toluene, ethanol and diethyl ether two times, respectively. The product was heated for 4 h at 383 K under vacuum and then immersed in 20 mL of toluene and 1.75 g (10.2 mM) of MBT was added. The mixture was stirred for 48 h under reflux conditions under a nitrogen atmosphere. The resulting MBT modified SiO_2 (MBT–SiO_2) was filtered off and washed with toluene, ethanol and diethyl ether, respectively. Finally, the resultant MBT–SiO_2 particles were heated for 4 h at 383K under vacuum.

2.4. Preparation of MBT–SiO_2 modified GCE

A commercial GCE (CH Instrument, diameter = 2 mm) were carefully polished with 0.3 μm alumina powder, and sequentially sonicated for 5 min in 1:1 nitric acid, 1 M NaOH, acetone and double-distilled water, respectively. 0.2 mg of MBT–SiO_2 microspheres was added into 0.5 mL of Milli-Q water, and sonicated for 5 min to obtain a uniform dispersion. A drop of the above solution was directly dispersed onto the fresh surface of GCE. After water evaporation, a thin MBT–SiO_2 film was formed on the electrode surface.

2.5. Preparation of Hg(II)-imprinted microporous PMBT film modified GCE

The prepared MBT–SiO_2 modified GCE was immersed into a 1.0 mM solution of Hg(II) for 15 min. The electrode was taken out, rinsed carefully with double-distilled water, and then dried under nitrogen flow at room temperature. Hg(II) ions were accordingly assembled onto the MBT–SiO_2 modified GCE through complexation interaction between the N and S atoms of MBT and Hg(II). The MBT–SiO_2 modified GCE with Hg(II) assembled on the electrode surface was immersed in the 60% DMF and 40% 0.05 M H_2SO_4 (v/v) electrolyte solution containing 5.0 mM MBT and 1.0 mM Hg(II). The electropolymerization was performed by nineteen consecutive cyclic scans in the potential range of 0.0 and +1.5 V at a scan rate of 25 mV s^{-1}. After the electropolymerization, the Hg(II)-imprinted poly(2-mercaptobenzothiazole)-SiO_2 (PMBT–SiO_2) films modified GCE was obtained. The Hg(II)-imprinted microporous PMBT films modified GCE (MPMBT/GCE) were further fabricated through the etching of the SiO_2 cores from PMBT–SiO_2 films with 5% aqueous HF. After dissolution of the SiO_2, Hg(II)-imprinted MPMBT/GCE were washed repeatedly with double-distilled water and immersed in a stirring solution containing 0.2 M HNO_3 at +0.8 V for ca. 60 s to remove residual Hg(II) templates. Then, the Hg(II)-imprinted MPMBT/GCE was rinsed with doubly distilled water and dried under nitrogen for further use. At the same time, the direct Hg(II)-imprinted PMBT films on GCE (PMBT/GCE) was also produced under identical chemical conditions. As a control, the non-imprinted microporous PMBT films modified GCE was prepared and treated in the same way except that the template Hg(II) ions were omitted from electropolymerization stage.

2.6. Electrochemical measurements

Hg(II) was chemically preconcentrated by immersing the Hg(II)-imprinted MPMBT/GCE in the solution (pH 5.0) containing Hg(II)