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Bisphenol A sensing based on surface molecularly imprinted, ordered mesoporous silica

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ABSTRACT

Molecularly imprinted, ordered mesoporous silica was synthesized using bisphenol A (BPA) as the template and 3-aminopropyltriethoxysilane modified with hexagonally structured mesoporous silica (SBA-15) as the carrier. Carbon paste sensors were constructed by mixing the molecularly imprinted, ordered mesoporous silica with graphite powder and paraffin oil, and they were found to detect bisphenol A (BPA) with enhanced selectivity due to their ordered mesoporous structure and their successful molecular imprinting. The linear range for the proposed sensor was 1.000×10^{-7} mol L^{-1} to 5.000×10^{-4} mol L^{-1}, and the detection limit was determined to be 3.222×10^{-8} mol L^{-1}. Overall, the sensor detected the water samples with satisfactory results.

1. Introduction

Mesoporous silica has been of considerable research interest since Mobil first proposed its use in 1992 [1]. It is proposed to possess the following characteristics: stability for synthesis, large, specific surface area and pore volumes [2,3], well-defined channels, hydrothermal stability [4], adjustable pore sizes [5], narrow size distribution [6] and easily functional. It is also known to provide more binding/active sites compared with traditional silica. By virtue of their high surface-to-volume ratio, mesoporous materials are capable of yielding excellent sensitivity via an enhanced interaction between the imprinted polymers and their analytes. Additionally, they have the potential to be an effective material to prepare electrochemical sensors with favorable performances.

Molecularly imprinted polymer (MIP), as a material for the sensors, can effectively overcome the interferences of other analyte species with the similar structures or functional groups and can improve the selectivity of a sensor [7,8]. Furthermore, a sensor based on MIP is stable, durable and can resist harsh conditions without loss of sensitivity [9].

Imprinted materials must have binding sites and a specific size and shape [10,11]. The binding sites and imprinted cavities also need to be embedded deep enough such that the substrate molecules cannot easily access to the molecularly imprinted polymer, which is synthesized by ordinary methods. This problem can be overcome by surface imprinted polymers, which have imprinted cavities located only on their surfaces [12]. Unfortunately, their stability of sorption is little weaker and sorption capacities are much lower [13]. On the other hand, this problem may also be overcome if we choose mesoporous silica as the support.

Bisphenol A (BPA), a type of estrogen present in the environment, can produce harmful effects on the endocrine systems of humans and wild animals [14–17]. It is widely used for the production of epoxy resins and polycarbonate plastics [18] and is currently found in baby bottles, plastic drinking bottles, dental seals, injection syringes, canned beverage drinks and metal food containers. Several methods have been developed for the determination of BPA; which are based on high-performance liquid chromatography (HPLC) and gas chromatography/mass spectrometry (GC/MS) [19–21] and are costly, time consuming and have elaborate pretreatments [22,23]. Therefore, it is necessary to seek a facile, cheap, stable and highly selective method to determine BPA.

In the quest for such a method, we investigated a novel BPA carbon paste electrode based on a surface molecular imprinting technology modified with mesoporous silica. The results showed that the electrochemical response toward BPA was remarkably reinforced by the molecularly imprinted mesoporous silica polymer (SBA-MIP) sensor. Additionally, it was shown that the selectivity of the SBA-MIP sensor was vastly improved over the ordinary silica imprinted polymer (SiO_2-MIP) sensor. The SBA-MIP sensor provided multiple active sites for direct oxidation of BPA and exhibited high performance, including wide linear-

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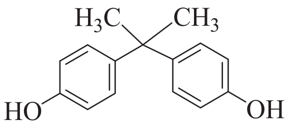

Fig. 1. Structure of bisphenol A.

ity, simple operation and good stability under the optimized conditions.

2. Experimental

2.1. Materials

Tetraethylorthosilicate (TEOS), 3-aminopropyltrimethoxysilane (APS) and silica (70–230 mesh) were purchased from Alfa; bisphenol A (BPA) (Fig. 1), 4-tert-butylphenol (BP) and triblock copolymer poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) (Pluronic P123; molecular weight 5800; $EO_{20}PO_{70}EO_{20}$) were obtained from Aldrich. Graphite powder and paraffin oil were purchased from the Chengdu Kelong Chemical Reagent Corporation Limited.

2.2. Apparatus

The CHI 660D and CHI 660B electrochemistry workstations (Shanghai CH Instruments, China), transmission electron microscopy (TEM) instrument (Tecnai 20, Phillips, Holand), S-4800 scanning electron microscope (SEM) (Hitachi, Tokyo, Japan), Quantachrome instruments (Boynton Beach FL, USA) and infrared spectrometer (Tensor 27, Bruker, German) were used as manufactured.

2.3. Synthesis of the SBA-MIP

The hexagonally structured mesoporous silica (Santa Barbara 15 SBA-15) material was synthesized according to a previously described procedure [24]. Amine-functionalized mesoporous silica was obtained by modification of SBA-15 with APS [25].

Synthesis of the MIP: BPA was dissolved in 50 mL of ethanol while stirring; 4.0 g of the amine-functionalized mesoporous silica was added and refluxed for 2 h, then 8 mL TEOS and 6 mL 1.0 mol L^{-1} AcOH were added. The mixture was stirred and refluxed for 8 h, and the product was filtered and dried under vacuum at 100 °C for 12 h. The product was washed twice with ethanol and once with ultrapure water; the remaining solid was extracted by a mixture of ethanol and 6 mol L^{-1} muriatic acid (v:v = 1:1) in a Soxhlet for 24 h, neutralized with 0.1 mol L^{-1} potassium hydroxide and washed by ultrapure water to remove the molecular template and any other excess polymer. Finally, the powder was dried at 100 °C for 12 h under vacuum. The resulting polymer powder (SBA-MIP) was collected using a standard analysis sieve (Fig. 2).

The non-imprinted functionalized mesoporous silica (SBA-NIP) was prepared using an identical procedure without adding BPA. MIP-SiO_2 and ordinary non-imprinted silica (NIP-SiO_2) were made by repeating the process and replacing SBA-15 with standard silica.

2.4. Preparation of the carbon paste sensor

SBA-MIP powder (0.027 g) was mixed with 0.153 g of graphite powder and 0.04 mL of paraffin oil in a carnelian mortar. The resultant homogenous carbon paste was tightly pressed into the end cavity of the sensor body (3 mm in diameter), and the surface was polished with a piece of smooth paper. The other sensors were prepared by the same procedure, but the SBA-MIP powder was replaced with graphite, SBA-NIP, SBA-15, SiO_2-MIP and SiO_2-NIP powder.

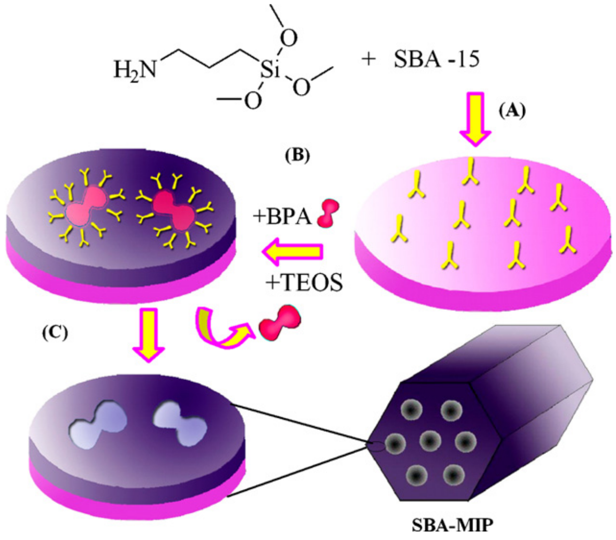

Fig. 2. Synthesis of SBA-MIP: (A) synthesis of the 3-aminopropyl functional mesoporous silica, (B) the process of imprinting and (C) the process of elution.

2.5. Electrochemical measurements

Unless otherwise described, the electrochemical experiments were performed in a conventional three-electrode electrochemical cell. The three-electrode system was comprised of a working electrode (the carbon paste electrode), a platinum wire (the auxiliary electrode) and a saturated calomel electrode (SCE). The cyclic voltammetry (CV) scan was performed from 0.1 V to 0.7 V (vs. SCE) at 100 mV s^{-1} and at a pH = 8.0 using a phosphate buffer as the determining medium.

3. Results and discussion

3.1. Characterization of the imprinting process

To determine the interaction between the recognition site and BPA, we studied the process of imprinted using Fourier transform-infrared (FT-IR) spectroscopy. A peak, which appeared around 1082.22 cm^{-1}, was representative of the Si–O–Si stretching vibrations. Silicon oxide (Si–O) vibrations were reflected around 801.77 and 464.08 cm^{-1}. The absorptions around 3442.70 and 1631.68 cm^{-1} resulted from O–H vibration, while peaks around 2925.86 and 1561.38 cm^{-1} manifested the C–H stretching and the N–H (primary amine) bending vibration, respectively. These results indicate that the $-NH_2$ group was successfully grafted onto the surface of mesoporous silica because the Si–OH signal was replaced with the Si–O–Si signal; the absorbance at 961.19 cm^{-1} had a large reduction. The absorption peaks of the imprinted and non-imprinted silicas appeared in similar locations because their major bands are similar [26,27].

3.2. N_2 adsorption/desorption experiments

Pore-size distributions, pore volumes, and BET isotherms were determined from nitrogen N_2 adsorption/desorption experiments. Typical N_2 adsorption/desorption isotherms and pore-size distributions are shown in Fig. 3 and Table 1. The results show that the surface area, pore volume and pore size of the SBA-MIP decreased drastically compared with SBA-15. The SBA-MIP was found to be microporous with a narrow pore-size distribution centered at