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RESEARCH PAPER

An Electrochemiluminescence Sensor with Molecularly Imprinted Polymer for Heroin Detection

SHANG Zhe-Yi, HAN Chao-Feng, SONG Qi-Jun*

The Key Laboratory of Food Colloids and Biotechnology, Ministry of Education, School of Chemical and Material Engineering, Jiangnan University, Wuxi 214122, China

Abstract: An electrochemiluminescence (ECL) sensor with molecularly imprinted polymer (MIP) film was developed for the detection of heroin. The sensor was prepared by re-modifying the molecularly imprinted polymer film onto $Ru(bpy)_3^{2+}$ modified glassy carbon electrode. The electrochemical and electrochemiluminescence behavior of the sensor was investigated. The proposed sensor displayed high sensitivity and excellent selectivity for the target molecule heroin. Under the optimal conditions (a scan rate of 100 mV s^{-1} and incubation time of 5 min in 0.1 M PBS), a linear response for heroin was achieved in the range of 1.0×10^{-14}–1.0×10^{-10} M with a detection limit of 4.0×10^{-15} M ($S/N = 3$). The sensor was successfully applied for the determination of heroin in urine and saliva with the recovery rates in the range of 97%–104%.

Key Words: Heroin; Electrochemiluminescence; Molecularly imprinted polymer; Sol-gel; Sensor

1 Introduction

Drugs not only cause serious damage to human health, but also induce a series of social problems. Heroin is one of the main drugs smoked and injected by addicts[1]. Current heroin detection methods mainly include differential pulse voltammetry[2], X-ray diffraction spectrum of principal component analysis (PCA)[3], competitive immunoassay[4], liquid chromatography (LC)[5,6], ion mobility spectrometry[7], nuclear quadrupole resonance pulse analysis[8] and electrochemiluminescence (ECL)[9,10]. The ECL based on Tris(2,2'-bipyridyl) ruthenium ($Ru(bpy)_3^{2+}$) was received widespread attention for its good controllability and high sensitivity. To avoid the waste of $Ru(bpy)_3^{2+}$ in liquid phase analysis, the reagent could be reused by immobilizing it on the electrode. Thus one could not only save the reagent and reduce the cost of testing, but also increase the anlytical sensitivity. Various methods, such as the Langmuir-Blodgett technique, self-assembly technique, polymer membrane technique, and sol-gel technique were developed for the $Ru(bpy)_3^{2+}$ immobilization[11]. Among these methods, cation-exchange immobilization by using Nafion as the exchanger was one of the most successful methods. The addition of carbon nanotubes (MWNTs) in Nafion can enhance the conductivity of the membrane and the MWNTs can also adsorb a certain amount of $Ru(bpy)_3^{2+}$ [12].

The ECL is often used as a detection method in combination with other separation methods. Although ECL has high sensitivity, the selectivity still cannot meet the needs of direct determination of actual samples. Therefore, to eliminate interferences in the analysis, a complicated pre-treatment of samples is often required, which causes the inconvenience in practical applications. Molecular imprinting technique is a novel method with high selectivity[13]. Molecular imprinted polymer (MIP) can enrich and separate target molecules in complex samples, which can not only eliminate the interferences within samples, but also further improve the sensitivity of the detection method[14]. In this study, an ECL sensor was prepared by combining ECL and MIP for the determination of heroin in human saliva and urine

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* Corresponding author. Email: qsong@jiangnan.edu.cn
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samples. The as-prepared sensor exhibited a very high sensitivity, good selectivity and reproducibility.

2 Experimental

2.1 Apparatus and reagents

The electrochemical measurements were performed on CHI660D electrochemical workstation (Shanghai Chen Hua instrument Co. Ltd, China). The ECL experiments were carried out on an MPI-E multifunction chemiluminescence analyzer (Xi'an Remax Electronic Science Tech. Co. Ltd, China). The VHX-100 Digital Microscope (Keyence, Japan) and S-4800 field emission scanning electron microscope (Hitachi, Co., Ltd, Japan) were used to observe the surface modification. A conventional three-electrode arrangement was used, including a platinum wire counter electrode, an Ag/AgCl (saturated KCl) reference electrode and a modified glassy carbon working electrode (diameter 4 mm, Tianjin Ida Hengsheng Co., Ltd). A homemade silica cell was used for the detection.

Multi-wall carbon nanotubes (MWCNTs, diameter 20–40 nm, length 5–15 μm, specific surface area 40−300 m^2 g^{-1}, purity ≥ 95%) were purchased from Shenzhen Nanotech. Port. Co. Ltd, China. Heroin hydrochloride was obtained from Institute of Forensic Science, Ministry of Public Security, China. Other reagents such as ethanol, hydrochloric acid, isopropanol, *N,N*-dimethyl formamide (DMF), potassium phosphate (KH_2PO_4) and potassium ferricyanide ($K_3[Fe(CN)_6]$) were of analytical grade and purchased from Sinopharm Chemical Reagent Co., Ltd., China. Tris(2,2'-bipyridyl) ruthenium(II) dichloride hexahydrate ($Ru(bpy)_3Cl_2·6H_2O$), Nafion (5% solution in a mixture of lower aliphatic alcohols and water) were purchased from Sigma-Aldrich (Milwaukee, WI, USA). Tetraethylorthosilicate (98%, TEOS), phenyltrimethoxysilane (99%, PTMOS) and methyltrimethoxysilane (99%, MTMOS) were purchased from Aldrich. Ultrapure water (> 18 MΩ cm) was produced by Heal Force Company's water purification equipment.

The $K_3[Fe(CN)_6]$ solution was prepared (5 mM $K_3[Fe(CN)_6]$ and 100 mM KCl). Phosphate buffer solution (PBS, 0.1 M, pH 7.0) was used as background electrolyte.

2.2 Fabrication of ECL-MIP sensor

Pretreatment of glassy carbon electrode was conducted by polishing the glassy carbon electrode with aluminium oxide (diameter 50 nm) on suede, followed by ultrasonic processing for 3 min in ultrapure water and ethanol respectively. Carbon nanotubes were carboxylated to prevent agglomeration[15]. A certain amount of carboxylated carbon nanotubes were dispersed in 0.1 mL *N,N*-dimethylformamide, then 0.8 mL isopropyl alcohol and 0.1 mL Nafion were added, and the mixture was mixed on a vortex mixer. Ultrasonic process was then adopted to form a stable dispersion. Based on this ECL electrode, we fabricated the ECL-MIP sensor with a sol-gel method reported in the references[17,18]. Some modifications and optimizations were carried out. In brief, an aliquot of 50 μL TEOS, 30 μL MTMOS, 28 μL PTMOS, 50 μL absolute ethyl alcohol, 10 μL 1 × 10^{-4} M HCl and 50 μL water were mixed and ultrasonically processed to obtain the non-imprinted sol-gel mixture. For molecularly imprinted sol, an aliquot of 10 μL 0.01 M heroin solution was added to 90 μL of above mixture and thoroughly mixed with vortex mixer. Then an aliquot of 3 μL the sol was dispersed on modified electrode surface, and dry at room temperature. After removal of the template molecule in pure water, the ECL-MIP sensor was obtained. Similarly, an ECL-nMIP sensor was also prepared with the sol in absence of the template molecules.

3 Results and discussions

3.1 Fabrication of ECL-MIT sensor

Nafion is a cation-exchanger, and $Ru(bpy)_3^{2+}$ can be readily adsorbed onto the composite membrane by the cation-exchange through Nafion membrane. However, the Nafion membrane can affect the conductivity of the glassy carbon electrode. To increase the conductivity of the film, Nafion was mixed with MWCNT, and applied on the glassy carbon electrode. Figure 1 is the cyclic voltammetry (CV) curves of the modified glassy carbon electrodes. The difference between the Figs.1a and 1b illustrated that the presence of Nafion is key to $Ru(bpy)_3^{2+}$ adsorption. Comparing Figs.1b and 1c, the addition of MWCNT could greatly enhance the conductivity of the modified electrode. Surface morphology of the modified electrode was characterized by scanning electron microscope (SEM), and the networks of carbon nanotubes were observed on the modified electrode (Fig.2A).

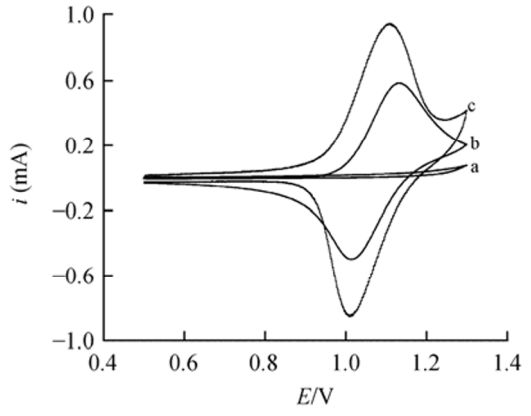

Fig.1 CVs of the GC electrode and modified GC electrodes in PBS (pH 7.0) solution

(a) GC electrode; (b) Nafion film modified electrode; (c) Nafion/MWCNT composite film modified electrode