A highly selective molecularly imprinted electrochemiluminescence sensor for ultra-trace beryllium detection

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HIGHLIGHTS

- A novel molecular imprinted electro-chemiluminescence sensor was fabricated for ultra-trace Be^{2+} detection.
- Imprint cavities in the MIPs from elution the Be–PAR complex could provide more recognition sites for analytes.
- ECL emission produced by the luminol–H$_2$O$_2$ ECL system, which was applied to detect Be^{2+}.
- It gave an extremely lower detection limit (2.35×10^{-11} mol L^{-1}) than the reported methods.

GRAPHICAL ABSTRACT

A novel molecular imprinted electrochemiluminescence sensor was fabricated for ultra-trace Be^{2+} detection with an extremely lower detection limit based on the luminol–H$_2$O$_2$ ECL system.
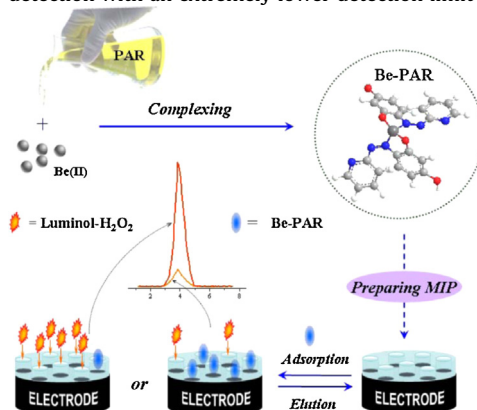
ABSTRACT

A new molecularly imprinted electrochemiluminescence (ECL) sensor was proposed for highly sensitive and selective determination of ultratrace Be^{2+} determination. The complex of Be^{2+} with 4-(2-pyridylazo)-resorcinol (PAR) was chosen as the template molecule for the molecularly imprinted polymer (MIP). In this assay, the complex molecule could be eluted from the MIP, and the cavities formed could then selectively recognize the complex molecules. The cavities formed could also work as the tunnel for the transfer of probe molecules to produce sound responsive signal. The determination was based on the intensity of the signal, which was proportional to the concentrations of the complex molecule in the sample solution, and the Be^{2+} concentration could then be determined indirectly. The results showed that in the range of 7×10^{-11} mol L^{-1} to 8.0×10^{-9} mol L^{-1}, the ECL intensity had a linear relationship with the Be^{2+} concentrations, with the limit of detection of 2.35×10^{-11} mol L^{-1}. This method was successfully used to detect Be^{2+} in real water samples.

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1. Introduction

Beryllium is an insidious carcinogenic poison due to its difficulty in biodegradation [1]. The general public is mainly exposed to trace amounts of beryllium via dietary intake. Water-soluble Be^{2+} may pose a serious threat to human health since it is

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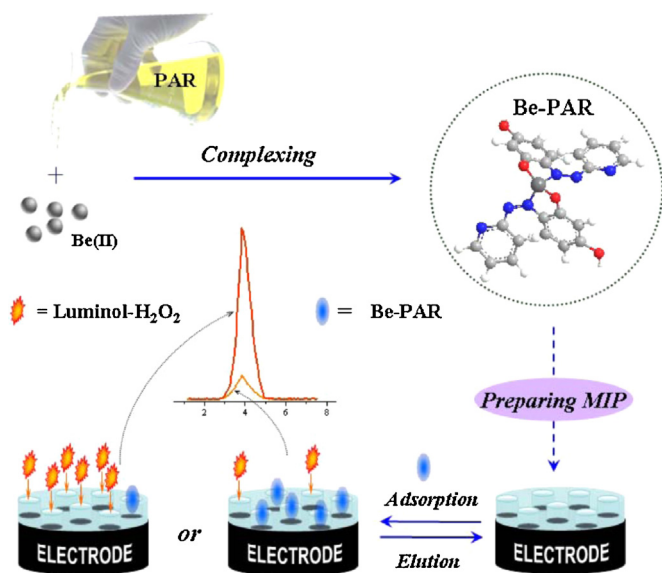
Scheme 1. Mechanism of recognization and measurement of the MIP sensor.

accumulated in the skin and soft tissue through food and water in one's daily diet. [3–5]. Be^{2+} is at trace levels in natural and waste waters [2], it can be detected through atomic absorption spectrometry [6], atomic emission spectrometry [7], and fluo-rospectrophotometry [8]. However, these methods either have insufficient sensitivity and selectivity, or need expensive apparatus and complicated sample pretreatment. Moreover, the detection might also be hindered by the interference compounds in samples. Thus, it is very important to develop highly sensitive and selective detection method for ultra-trace beryllium in water and food samples.

MIP are nanoporous polymeric material that can selectively recognize target molecules [9–11], which is called the template molecule. They have been used a lot in chromatography [12], sensors [13], and solid-phase extraction [14] for its good selectivity. MIP-based sensors are widely employed to detect organic compounds and biomacromolecules [11,15–19]. However, it could also be used for the determination of metal ions, such as Cu^{2+} [20], Pb^{2+} [21], Eu^{3+} [22], Hg^{2+} [23], Zn^{2+} [24], and other metal ions [25]. But Be^{2+} detection using molecularly imprinted polymer sensor has not been reported yet.

ECL sensors have good sensitivity [26]. MIP sensors via ECL measurement could facilitate the highly sensitive and selective detection with a relatively simple sample pretreatment procedure [27,28]. This study is the first to fabricate a MIP–ECL sensor for ultra-trace Be^{2+} determination. The complex molecule was used as the template molecule to copolymerize with the functional monomer and form the MIP. After the elution of the complex from MIP, the imprinted cavities formed could act as the tunnel for probe to reach the surface of the electrode and produce ECL. When the MIP-electrode was immersed in samples with PAR, the complex was specifically recognized by the cavities through the space size and the binding sites. With the cavities retaken by the complex molecules, the ECL intensity decreased. The mechanism of the sensor is shown in Scheme 1.

2. Experimental

2.1. Apparatus and reagents

ECL measurement was carried out using an ECL analysis system (MPI-E, Xi'an Remax Analysis Instrument Co., Ltd., Xi'an, China).

Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were performed on an electrochemical workstation (CHI 660D, Shanghai Chenhua Instrument Co., Ltd., Shanghai, China). The classic three-electrode system consisted of a MIP-modified Au electrode (2 mm diameter) as the working electrode, a potassium chloride-saturated Ag/AgCl electrode as the reference electrode, and a Pt wire electrode as the auxiliary electrode. pH measurements were conducted using a PHS-3D digital pH meter (Shanghai Precision & Scientific Instrument Co., Ltd., Shanghai, China). The infrared (IR) assay was performed on a Nicolet iS10 (Thermo Fisher Scientific, USA).

PAR, o-phenylenediamine (o-PD), trishydroxymethyl amino-methane (Tris), $BeSO_4\cdot4H_2O$, acetic acid, and sodium acetate were purchased from Sinopharm Chemical Reagent Co., Ltd., Shanghai, China. Luminol (>98%) was obtained from Yingrun Biotechnologies Inc., Changsha, China. The luminol stock solution (1×10^{-3} mol L^{-1}) was prepared by dissolving 0.177 g luminol in 0.1 mol L^{-1} NaOH solution and stored in the dark for further use. The H_2O_2 stock solution (3×10^{-3} mol L^{-1}) was stored in a refrigerator for further use. A Tris–HCl buffer solution (0.05 mol L^{-1}, pH 7.8) was prepared by adjusting the pH of a 0.1 mol L^{-1} Tris solution by adding a 0.1 mol L^{-1} HCl solution. All other reagents were analytical grade and were used without purification. Ultrapure water obtained from a water purification system (>18 $M\Omega$; Youpu Super Water Co., Ltd., Chengdu, China) was used to prepare the solution.

2.2. Preparation of the Be–PAR complex

According to related references [29,30], PAR (0.42 g) was dissolved in ethanol (120 mL) at 50 °C and then added with 0.17 g of $BeSO_4\cdot4H_2O$. NaOH (0.1 mol L^{-1}) was dropped into the solution under stirring until flocs formed. The solution was stirred for 4 h at a constant temperature and then allowed to cool to room temperature overnight before filtration. The precipitate was washed thrice with ethanol and then vacuum-dried at 40 °C for 12 h to yield the Be–PAR complex. This complex was characterized by IR spectrometry. The curves compared with PAR are shown in Fig. 1. The N=N stretching vibration of the Be–PAR complex red-shifted from 1479 cm^{-1} to 1469 cm^{-1} probably because of the electron-drawing effect from the metal ion. A strong wide adsorption peak belonging to the hydroxyl group appeared around 3600–3200 cm^{-1}, and an association peak appeared around 2700–3100 cm^{-1} in PAR. The hydroxyl group
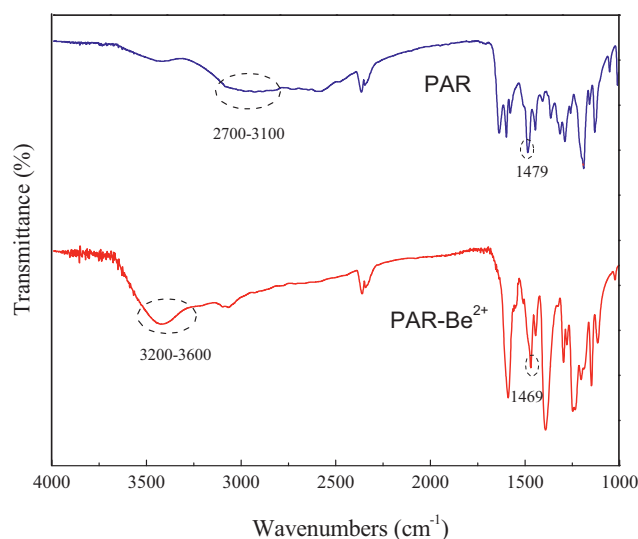

Fig. 1. IR spectra of the PAR and Be–PAR complex.