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Electrochemical sensor based on in situ polymerized ion-imprinted membranes at graphene modified electrode for palladium determination

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ABSTRACT

In this work, an amperometric sensor was developed for the selective recognition and sensitive determination of palladium in complex matrices using a glassy carbon electrode (GCE) modified with a novel ion-imprinted membrane (IIM) and graphene. Graphene enhanced the sensor's electron transfer and sensitivity. The electrode surface was first directly modified with graphene through the electrodeposition of graphene oxide. An ion-imprinted polymer membrane was subsequently synthesized on this modified surface via in situ polymerization in acetonitrile using allylurea (NAU) as a functional monomer, ethylene glycol dimethacrylate (EGDMA) as cross-linking agent, and azobisisobutyronitrile as an initiator at a molar ratio of template ($PdCl_2$) to NAU to EGDMA of 1:4:40. Amperometric *i-t* curves were measured for the determination of palladium. The designed modified electrode was shown a linear response to Pd(II) ions in the range of 2.0×10^{-8}–2.0×10^{-4} mol L^{-1} of Pd(II) ion with a detection limit of 6.4×10^{-9} mol L^{-1}. Metal ions present at concentrations 15 times higher than that of Pd(II) did not interfere with the determination of Pd(II). The sensor was successfully applied to determine palladium in catalyst and plant samples with a relative standard deviation (RSD) of less than 3.3% ($n = 5$) and recoveries in the range of 99.2–106.5%.

1. Introduction

Palladium is an important material for modern technologies related to spaceflight, aviation, and auto manufacturing. And it is often used along with platinum and rhodium worldwide in vehicles as catalysts to reduce emissions of gaseous pollutants such as carbon monoxide, nitrogen oxides, and hydrocarbons [1]. Currently, an increasing number of cars are being equipped with catalytic converters containing these novel anthropogenic metals. Although the benefits of catalysts are indisputable, they release highly toxic elements including platinum, rhodium, and palladium into the atmosphere during their use. These elements are being found at increased levels in environmental matrices, especially in soils, plants, road sediments, and airborne particles [2,3], increasing health and environmental risks. Therefore, it is very essential for monitoring pollution of palladium ions (Pd^{2+}) in environmental samples and biological matrices. To date, Pd^{2+} can be rapidly and sensitively detected by different methods, such as spectrophotometry [4,5], atomic absorption spectrometry (AAS) [6–8], inductively coupled plasma mass spectrometry (ICP-MS) [9,10], inductively coupled plasma optical emission spectrometry [11,12], and high performance liquid chromatography (HPLC) [13,14]. However, electrochemical methods are more desirable for the detection of Pd^{2+} because they exhibit easier and cheaper, less labor intensive and highly sensitive relative to those developed methods [15]. Several stripping voltammetric methods are in existence for the analysis of Pd^{2+} in aqueous solutions, most of which utilize hanging mercury drop electrode as working electrode and demand a stringent process of sample pretreatment [16,17]. The method, relying on toxic mercury, raises safety and environmental concerns. Therefore, an inexpensive, highly sensitive and non-toxic electrode is an ideal probe for palladium analysis. A previous study used electrochemical sensor for the detection of Pd^{2+} in spiked environmental water and soil samples by Molecular Imprinting Technology (MIT) [18].

MIT, which is as an established method for the preparation of polymeric materials such as molecular/ion-imprinted polymers (MIPs/IIPs), has become an effective analytical tool [19–21]. The molecular/ion imprinting process introduces recognition properties into synthetic materials through the use of appropriate template molecules. So, the obtained MIPs/IIPs contain complementary surface features from these template molecules and are highly selective for the recognition of these template molecules over structurally similar compounds. This advantage combined with its other advantages over biological recognition elements including their increased stability, reusability, and simplicity and their lower cost makes MIPs/IIPs ideal recognition elements in sensors [22,23]. Several sensors have been constructed based on IIPs for the determination of metal ions such as Cd^{2+} [24], Zn^{2+} [25], Ce^{4+} [26], Cu^{2+} [27], Pb^{2+} [28,29], and Hg^{2+} [30].

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Bojdi et al. [18] developed a stripping voltammetric determination of palladium ions by a carbon paste electrode modified with palladium imprinted polymer. Although the detection limit (LOD) of this method was very low, the preparation process of the imprinted sensor was more complex, which needed to preparation of the imprinted polymers firstly, then used the polymers modified carbon paste electrode. In our study a Pd(II) ion-imprinted sensor was designed by simple and convenient in situ polymerization one-step synthesis method. Meanwhile, considering that graphene with large specific surface area, high chemical stability, and high electrical conductivity [31,32], our workgroup used it to modify the electrodes to improve sensor response, increase sensitivity, and decrease detection limits.

In this work, the advantages of graphene, IIPs and electrochemical methods were combined to design a highly sensitive and selective ion-imprinted sensor for the detection of palladium. The surface of a glassy carbon electrode (GCE) was directly modified with graphene (G) via the electrodeposition of graphene oxide (GO). A Pd(II) ion-imprinted membrane was subsequently formed on the surface of the G/GCE by in situ polymerization in acetonitrile using allyluread (NAU) as a functional monomer, ethylene glycol dimethacrylate (EGDMA) as a cross-linking agent, and azobisisobutyronitrile (AIBN) as an initiator. To the best of our knowledge, this is the first reported use of NAU for the preparation of a Pd(II) ion-imprinted membrane. NAU was able to coordinate with Pd(II) by using two of its nitrogen atoms as donor atoms according to the Lewis theory of acids and bases (HSAB theory). The electrochemical performance of the developed IIP sensor was investigated using cyclic voltammetry (CV) and amperometry. Moreover, the sensor was employed for the detection of Pd(II) in catalyst and plant samples.

2. Experimental

2.1. Apparatus and instrumentation

Electrochemical data were obtained with a three-electrode system using CHI 660D electrochemical workstation (Shanghai CH Instruments Co., China) and 797 VA Computrace (Metrohm, Switzerland). A three electrode cell (10 mL) with an ion-imprinted membrane modified glassy carbon electrode as working electrode, a saturated calomel electrode (SCE) as reference electrode and a platinum wire electrode as counter electrode was used. All potentials were measured and reported versus SCE. Prior to modification, the glassy carbon electrode (GCE, 3 mm diameter) was firstly polished with 0.5 μm and 50 nm alumina slurry, successively rinsed thoroughly with absolute alcohol and water in ultrasonic bath, and then dried in air.

2.2. Reagents and chemicals

$PdCl_2$, H_2PtCl_6, $RhCl_3 \cdot 3H_2O$ and $IrCl_3 \cdot nH_2O$ were obtained from Kunming Institute of Precious Metals (Yunnan, China). Allylurea (NAU), 2-acetamidoacrylic acid(AAA),2-(allylthiol) nicotinic acid (ANA) and acrylamide (AM) were purchased from Sigma Aldrich (St. Louis, MO, USA). Ethylene glycol dimethacrylate (EGDMA) was purchased from Suzhou Anli Chemical Factory (Jiangsu, China) and distilled under vacuum to remove the stabilizers prior to use. Azobisisobutyronitrile (AIBN) was purchased from Shanghai Reagent Factory (Shanghai, China) and purified by recrystallization from ethanol before used. The other reagents and solvents were purchased from Tianjin Kemiou Chemical Reagent Co., Ltd. (Tianjin, China).

The stock solution (1.0×10^{-2} mol L^{-1}) of Pd(II), Pt(IV), Rh(III) and Ir(III) were prepared by dissolving appropriate amount of $PdCl_2$, H_2PtCl_6, $RhCl_3 \cdot 3H_2O$ and $IrCl_3 \cdot nH_2O$ in 5.0 mL of 2.0 mol L^{-1} HCl and then diluted to 100 mL with de-ionized water, respectively. The stock solution (1.0×10^{-2} mol L^{-1}) of the other metal ions used in this work was prepared with their nitrate or chloride. The working standard solution was obtained by diluting the stock solution with de-ionized water. The supporting electrolyte was phosphate buffer solution (pH 5.29), which was prepared with $KH_2PO_4 \cdot 2H_2O$ and $Na_2HPO_4 \cdot 12H_2O$.

The reagents and solvents used without special illustration were of analytical reagent grade and used without further purification. De-ionized water was produced by a Millipore water system composed of Milli-RO 60 and Milli-Q SP.

2.3. Preparation of sample solution

2.3.1. Treatment of the leaves sample solutions

About 100 g of leaves were collected from the *Cinnamomum pedunculatum* in 121 street of Kunming (Yunnan, China). The leaves were firstly washed with detergent, tap water and de-ionized water successively, and then dried at room temperature for 24 h followed by drying at 90 °C for 4 h. After that, 5.0000 g of the pulverized leaves was immersed with 10 mL of nitric acid for 12 h in a conical flask covered with a short neck funnel, and then heated at 140 °C until the volume of solution was less than 1 mL. 5 mL of aqua regia was added. The mixture was heated at 160 °C to near dryness and the residue was dissolved with 5 mL of de-ionized water by boiling for 10 min. After cooling to room temperature, the solution was filtered, and the filtrate was diluted to 25 mL with de-ionized water.

2.3.2. Preparation of the catalyst sample solutions

After the catalyst materials were ground to pass through a 200 mesh size sieve to facilitate sample dissolution, 25.0 mg of samples was weighed accurately into a Teflon high-pressure microwave acid digestion bomb and 5.0 mL of concentrated nitric acid, 4.0 mL of hydrochloric acid and 10.0 mL of 30% hydrogen peroxide were added. The bomb was sealed tightly and then positioned on the carousel of the microwave oven. The system was operated at 600 W and 350 psi with a heating program as 120 °C (5 min, hold 2 min), 180 °C (6 min, hold 10 min). The digest was evaporated to near dryness. The residue was dissolved with 2 mL of 2.0 mol L^{-1} HCl and then diluted to 25 mL with de-ionized water.

2.4. Preparation of graphene modified electrodes

Graphene oxide (GO) was prepared using a modification of Hummers and Offeman's method from graphite powders [33]. 1.0 g of graphite powder was added into 50 g of NaCl powder and then grinded homogeneously. After that, the mixture was dissolved completely with water and then filtered. 23 mL of H_2SO_4 was added to the filter

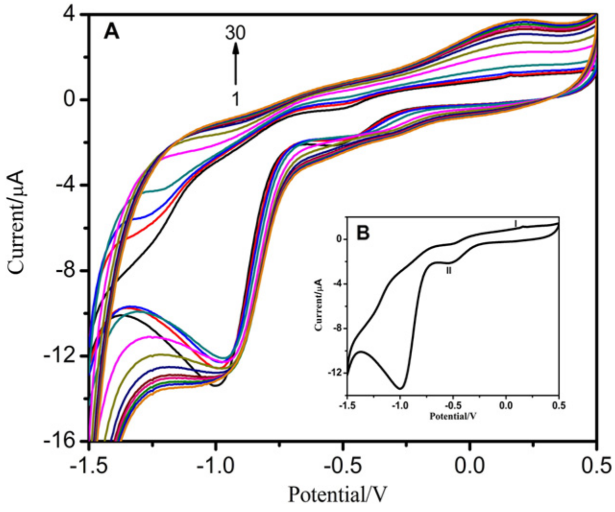

Fig. 1. Cyclic voltammograms of electrodeposition process of graphene on GCE. A: thirty cycles; B: the first cycle.