Determination of Nanomolar Lead (II) 
Using H$_2$O$_2$-Oxidized Activated Carbon Modified Electrode

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Abstract—The virgin activated carbon (AC) was oxidized by 30% H$_2$O$_2$ under the ultrasonic condition for 6 h (denoted as AC–6). The electrochemical response of Pb$^{2+}$ at the AC–6 modified paste electrode was investigated, suggesting that AC–6 shows much higher accumulation efficiency to trace levels of Pb$^{2+}$. Based on this, a sensitive and convenient electrochemical method was developed for the determination of Pb$^{2+}$ utilizing the excellent properties of AC–6. In pH 3.6 HAc–NaAc buffer, Pb$^{2+}$ was easily accumulate at the surface of AC–6 modified paste electrode, then reduced to Pb at $-1.20$ V. During the following anodic sweep, the reduced Pb was oxidized and resulted in an oxidation stripping peak at $-0.58$ V. The stripping peak current is proportional to the concentration of Pb$^{2+}$ over the range from the $8.0 \times 10^{-9}$ to $2.0 \times 10^{-6}$ mol l$^{-1}$, and the limit of detection is as low as $2.0 \times 10^{-9}$ mol l$^{-1}$. Finally, this newly-developed method was successfully employed to determine Pb$^{2+}$ in water samples.

Key words: Pb$^{2+}$, determination, activated carbon, modified electrode, electrochemistry 

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INTRODUCTION

It is of great importance and interest to develop a sensitive, selective and simple method for the determination of Pb$^{2+}$ since it is a common toxic metal industrial pollutant and can cause a diversity of severe diseases such as digestive, neurological, and mental troubles. Among various methods for Pb$^{2+}$ analysis, electrochemical method attracts increasing attention because it is considered to be sensitive, accurate, fast and convenient. For metal ion determination, anodic stripping voltammetry (ASV) is an ideal electroanalytical technique due to the higher sensitivity and excellent resolution ability. In the past, different mercury electrodes including dropping mercury electrode (DME), hanging drop mercury electrode (HMDE) and mercury film electrode (MFE) were extensively used in ASV since mercury electrode possesses many advantages such as high sensitivity, excellent reproducibility and easy surface renewal. However, many efforts have been made to develop mercury-free electrode for replacement of mercury electrode because mercury is also toxic and can cause many adverse effects.

Carbon paste electrode (CPE), invented by Adams at the end of the 1950s, is a mixture of an electrically conducting graphite powder and a pasting liquid. Till now, CPE has obtained considerable attention and widely used in electrochemistry because of the following unique properties: porous surface, wide potential range, easy preparation, convenient surface renewal, low residual current and low cost. To date, all kinds of CPEs have been reported for the determination of Pb$^{2+}$ [3–10]. However, to the best of our knowledge, electrochemical determination of trace levels of Pb$^{2+}$ using an H$_2$O$_2$-oxidized activated carbon paste electrode has not been reported.

The aim of the current study is to develop a sensitive and convenient electrochemical method for the determination of Pb$^{2+}$ utilizing the excellent properties of oxidized activated carbon. Activated carbon is a carbon-based material with porous structure, large surface area and strong adsorptive ability. In order to further improve the properties of activated carbon, introduce unique characterization and also to expand its application in electrochemistry, the pristine activated carbon was treated by 6-h successive ultrasonic oxidation in H$_2$O$_2$. It is found that the H$_2$O$_2$-oxidized activated carbon exhibits much larger surface, much more pores and higher accumulation ability toward Pb$^{2+}$. As a result, the electrochemical response of Pb$^{2+}$ was remarkably improved and the stripping peak current significantly enhances at the H$_2$O$_2$-oxidized activated carbon paste electrode.

EXPERIMENT

Reagents

Stock solution of $1.00 \times 10^{-2}$ mol l$^{-1}$ Pb$^{2+}$ was prepared by dissolving Pb(NO$_3$)$_2$ in redistilled water, and then diluted to working solution at desired concentra-

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tion by redistilled water. Activated carbon, paraffin oil and graphite powder (spectral reagent) were purchased from Sinopharm Group Chemical Reagent Co., Ltd, China. Other chemicals used were of analytical reagents, and all the chemicals were used without further purification.

**Apparatus**

All the experiments were carried out using a VersaStat II Potentiostat/Galvanostat (Princeton Applied Research, USA), which was controlled by a PC using the Powersuit Software.

A conventional three-electrode system, consisting of an oxidized activated carbon paste working electrode, a saturated calomel reference electrode (SCE) and a platinum wire auxiliary electrode, was employed.

Atomic absorption spectrometric measurements were conducted with AA–6300 atomic absorption spectrophotometer.

**Oxidative Treatment of Activated Carbon**

The oxidation treatment of activated carbon was performed according to the following procedure: 2.0 g of activated carbon was added into 30.0 ml 30% H2O2, then ultrasonicated for 6 h at room temperature. After that, the oxidized activated carbon (denoted as AC–6) were collected on a filter membrane with the pore size of 25 nm, and then washed with redistilled water for several times. Finally, the washed AC–6 were collected and dried at 100°C.

**Preparation of AC–6 Modified Paste Electrode**

The electric conductivity of both AC and AC–6 is very poor. In order to overcome this drawback, the AC–6 modified paste electrode was prepared by homogeneously mixing 15.0 mg AC–6, 85.0 mg graphite powder and 30.00 µl paraffin oil in a carnelian mortar to form a uniform AC–6 paste. After that, the paste was pressed into the end cavity (3 mm in diameter, 1 mm in depth) of working electrode body, and the surface was smoothed against a weighing paper.

The AC modified paste electrode was prepared by the same procedure except that the AC–6 was changed to AC. The unmodified paste electrode (that is graphite paste electrode) was prepared according to the above-described method but without AC–6.

**Analytical Procedure**

Unless otherwise stated, 0.1 mol l–1 HAc–NaAc with pH of pH 3.6 was used as supporting electrolyte Pb2+ analysis. The analytical procedure mainly includes two steps: accumulation step and determining step. Firstly, Pb2+ was accumulated at the surface of AC–6 modified paste electrode, and then reduced to Pb at –1.20 V. Secondly, the reduced Pb was oxidized to Pb2+ during the anodic potential sweep from –1.20 to –0.30 V, resulting in an oxidation stripping peak at –0.58 V, which measured as the analytical signal for Pb2+.

After each measurement, the used AC–6 modified paste was carefully removed from the end cavity and another new AC–6 modified electrode was fabricated again.

**RESULTS AND DISCUSSION**

**Electrochemical Response of Pb2+**

Figure 1 shows the anodic stripping voltammetric responses of 5.0 × 10–7 mol l–1 Pb2+ at different working electrodes in pH 3.6 HAc–NaAc buffer (0.1 mol l–1). After 2 min accumulation under –1.20 V, an oxidation stripping peak appears at the unmodified paste electrode (i.e. graphite paste electrode) during the square wave sweep from –1.20 to –0.30 V (curve a). The stripping peak locates at –0.58 V, and the peak current is relatively low.

Figure 1b illustrates the square wave anodic stripping voltammograms of 5.0 × 10–7 mol l–1 Pb2+ at the AC-modified paste electrode. After 2 min accumulation, an oxidation stripping peak is observed at –0.58 V. Compared with curve (a), it is found that the stripping peak current of Pb2+ increases slightly at the AC-modified paste electrode. This may be attributed to the fact that AC exhibits larger surface area and stronger adsorption ability to Pb2+.

To one’s interesting, the anodic stripping peak current of 5.0 × 10–7 mol l–1 Pb2+ significantly increases at the AC–6 modified paste electrode (curve c). Furthermore, the stripping peak becomes well-shaped. When