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Highly ordered platinum-nanotube arrays for oxidative determination of trace arsenic(III)

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ABSTRACT

A novel method for the oxidative determination of trace arsenic(III) was investigated on highly ordered platinum-nanotube array electrodes (PtNTAEs). The PtNTAEs with a highly organized structure were fabricated by electrochemical deposition of platinum in a 3-aminopropyltrimethoxysilane-modified porous anodic alumina template (PAA). The morphologies and structures of PtNTAEs were characterized by scanning electron microscopy (SEM) and X-ray diffraction (XRD). Electrochemical experiments proved that the PtNTAEs exhibited better performance for As(III) analysis in comparison with platinum nanoparticles-coated GCE (Pt_{nano}/GCE) or Pt foil electrode. The PtNTAEs showed to provide higher reproducibility and lower detection limit. The relative standard deviation (RSD) was 3.5% for 50 repeated measurements of 20 μM As(III), and the limit of detection (LOD) was 0.1 ppb, which was typically 1–2 orders of magnitude lower than that of Pt_{nano}/GCE or Pt foil electrode.

1. Introduction

The detection of trace amounts of arsenic in contaminated groundwater is a subject that has become increasingly important in recent years. Long-term exposure to arsenic via drinking water can cause a variety of health problems [1]. Many spectroscopic methods have been developed for the determination of arsenic, as summarized in recent reviews [2–4]. However, these techniques are time-consuming, labor intensive and involving expensive instrumentation [5]. Then the equipment is not easily deployed in the field.

Electrochemical techniques for detecting As(III) has recently come to the forefront of research as a possible means, mainly due to its rapid analysis, low-cost instrumentation, simple operation and the ability to measure low concentrations of metal ions at the ppb levels [6]. Different electrode, such as mercury [7,8], gold [9–11], silver [12], platinum [13–16], were used to detect arsenic by stripping voltammetry. However, due to the potential toxicity of mercury together with operational limitations, mercury electrodes were subsequently replaced by solid substrates [17]. Gold-based electrodes suffered major setbacks: lengthy analysis time (15–20 min for the deposition of arsenite), poor response precision and stability using anodic stripping voltammetry (ASV) [5]. Although there have been several reports about oxidative detection of As(III) on Pt electrodes, the sensitivity of such methods was not satisfactory. Considering arsenic's toxic character, there is still growing interest for new, sensitive methods that can be satisfactorily employed for the reliable measurements of trace arsenic.

Recently, metal nanotubes are gaining popularity due to their versatile and important properties including high aspect ratio, chemical stability, extremely high mechanical strength and a large specific surface area [18]. They have attracted great attention in many applications such as catalysis [19], biomaterials [20], microelectronics [21] and photronic materials [22]. PAA template has been demonstrated to be a very versatile and economic method for fabricating different nanotubes, mainly due to its predominant properties such as uniform and well-aligned pores, high temperature and chemical resistance and a large range of pore diameter distribution (10–300 nm) [23]. However, to our best knowledge, no paper about metal nanotubes for voltammetric detection of heavy metals has been reported.

In this study, for the first time, the oxidative detection of As(III) on highly ordered platinum-nanotube array electrodes by anodic scan voltammetry was investigated. The PtNTAEs were fabricated by electrochemical deposition of platinum in 3-aminopropyltrimethoxysilane-modified PAA template, and characterizations of the resulting PtNTAEs were performed by SEM, XRD and cyclic voltammetry. The PtNTAEs were successfully applied to detect As(III) with improved performance.

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2. Experimental

2.1. Materials and chemicals

All the chemicals were of analytical grade. $H_2PtCl_6 \cdot 6H_2O$ (99.9%), $K_4[Fe(CN)_6]$, $K_3[Fe(CN)_6]$, H_2SO_4 (<100 ppt arsenite, environmental grade), H_3BO_3, NaOH and 3-aminopropyltrimethoxysilane (APS, 95%), were purchased from Aldrich (Sigma–Aldrich, Germany) and used without further purification. Arsenite standard solution (1000 mg/L) in HNO_3 was purchased from Merck (Merck, Germany) and diluted to obtain appropriate concentrations of arsenite. PAA templates were purchased from Whatman International Ltd. (Maidstone, UK). All solutions were prepared using Milli-Q (Millipore, Bedford, MA) A-10 gradient (18 MΩ cm) deionized water.

2.2. Instrumentations

Electrochemical measurements were performed with a CHI660a electrochemical workstation (Chenhua Instrumental Corporation, China), in connection with a computer. A modified glassy carbon electrode (geometric area of 0.07 cm^2, BAS Co., Japan) served as working electrode, with a saturated calomel electrode (SCE) and a platinum wire acting as reference electrode and counter electrode, respectively. The morphology of PtNTAEs was characterized by scanning electron microscopy (JSM-6360LV, Hitachi, Japan) with an accelerating voltage of 20 kV. X-ray diffraction measurements were performed using a diffractometer (model D/max 2550V, Rigaku Co., Japan) with radiation of a Cu target (Kα, $\lambda = 0.15406$ nm) to determine the crystal structure.

2.3. Preparation of Pt-nanotube arrays

Before the experiments, bare GC electrode was mechanically polished with alumina (0.05 μm) slurry until a mirror like surface was obtained, then sonicated with acetone, ethanol and doubly distilled water, respectively.

The procedure for preparing PtNT array was described as follows: first, a thin layer of Au was deposited by vacuum evaporation onto the branched side of the PAA template. Next, for synthesizing platinum-nanotubes, a GC working electrode was constructed in contact with the Au-coated side of alumina membrane by epoxy resin. Then the pore walls of the alumina membrane were silanized by immersing the preprocessed electrode in a 1 vol% solution of 3-aminopropyltrimethoxysilane for 30 min resulting in amino-derivatized pore walls [24]. Electrodeposition of platinum in the modified PAA templates was achieved in a three-electrode electrochemical cell with the bare side of the alumina membrane facing a solution containing 8.23 mM $PtCl_6^{2-}$ and 30 g/L H_3BO_3 solution under constant N_2 ambient, followed by a constant-potential deposition at −0.1 V for several minutes. Finally, the prepared electrodes were immersed in a 3 M NaOH solution for 10 min to remove the PAA template, and then carefully rinsed several times with distilled water. The preparation of Pt_{nano}/GCE for oxidative detection of As(III) was described in details in reference reported by Dai and co-workers [15].

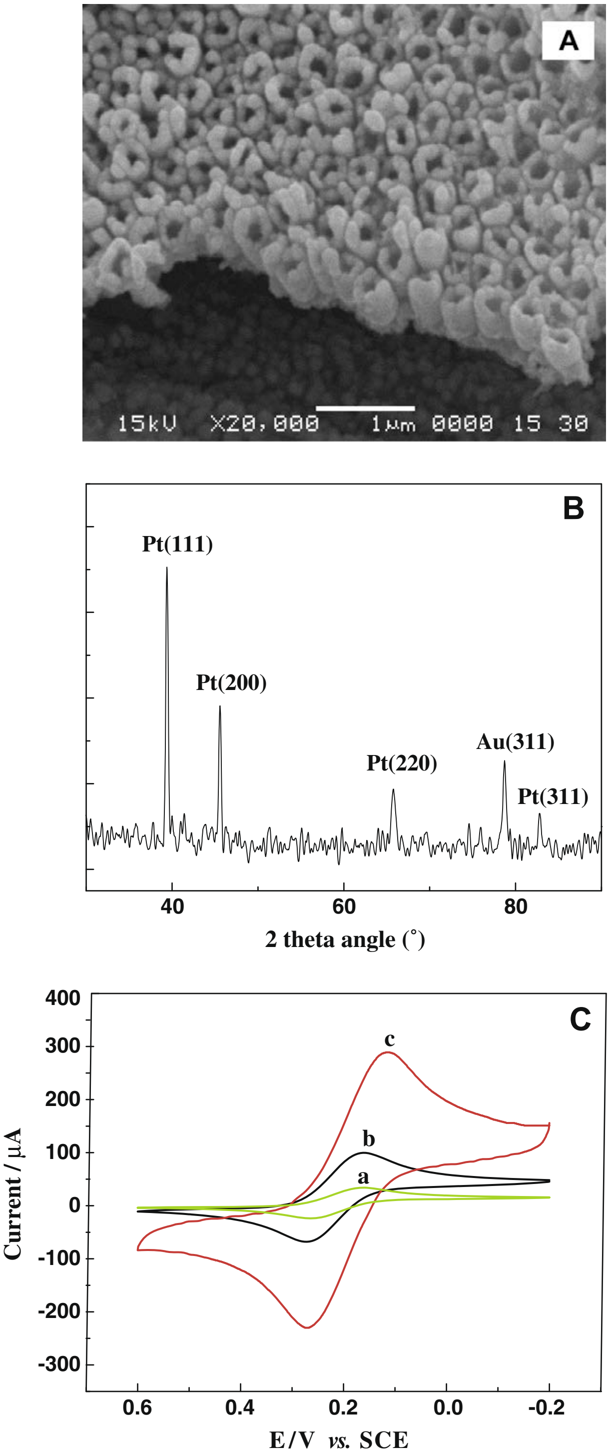

Fig. 1. SEM image of cross-sectional view (A) of the PtNTAEs; (B) X-ray diffraction (XRD) pattern of the PtNTAEs after annealing; (C) Cyclic voltammetries of (a) Pt foil electrode, (b) Pt_{nano}/GCE, and (c) PtNTAEs in 20 mM $[Fe(CN)_6]^{3-/4-}$ and 0.2 M KCl with scan rate of 20 mV/s.

3. Results and discussion

3.1. Characterization of PtNTAEs

Fig. 1A represents SEM image of cross-sectional view of the PtNTAEs, where the well-ordered and relatively uniform Pt-nanotube arrays were observed. The diameters of nanotubes were ca. 300 nm with their length of ca. 700 nm.

For further characterization of the structure of the patterned material, the XRD measurement of the PtNTAEs was carried out. Fig. 1B shows diffraction peaks at 111, 200, 220 and 311 pertaining to face-centered cubic (fcc) of Pt crystal structure, which was prepared from nanotube arrays of platinum after it was annealed at 500 °C under a nitrogen atmosphere for 5 h. The observed Au(3 1 1) XRD peak was due to the sputtered gold film which