Carbon nanofiber electrode array for the detection of lead

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ARTICLE INFO

ABSTRACT

A nanoelectrode array of vertically aligned carbon nanofibers was evaluated for the detection of Pb^{2+} by anodic stripping voltammetry. The achieved detection limit of 1.73 nM is well below the environmental guidelines. The approach provides a safer alternative to the mercury electrodes commonly used for the detection of heavy metals.

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1. Introduction

Lead (Pb^{2+}) is a well-known non-degradable pollutant in the environment that can accumulate in the human body through the food chain and lead to adverse effects on immune, reproductive and central nervous systems [1]. The presence of Pb^{2+} in some city water supplies with lead service pipes has received considerable attention recently [2]. Pb^{2+} can enter drinking water when these pipes corrode, especially when the water is high in acidity or has a low-mineral content [3]. Thus, it is crucial to develop analytical techniques for the routine and effective monitoring of Pb^{2+}.

Electrochemical stripping analysis has long been recognized as a powerful tool for measuring trace metals [4]. Its notable sensitivity is credited to an effective pre-concentration step with advanced measurement procedures that generate an extremely favorable signal-to-background ratio [5]. Mercury film and hanging mercury drop electrodes have been routinely used as working electrodes in anodic stripping voltammetry (ASV) [6]. Mercury's high overvoltage for hydrogen and its ability to form metal amalgams enable pre-concentration of many important metals at the electrode, giving rise to well defined stripping peaks and low detection limits. However, the toxicity of mercury limits its use, which has promoted searches for alternative electrode materials that perform as well as mercury [7–20].

Carbon based nanoelectrodes are an alternative explored for this particular application due to their large specific surface area, mechanical robustness and wide potential window [12,13]. Nanocomposite electrodes made of carbon nanofibers, modified glassy carbon electrodes and various others have been used for the detection of heavy metals [14–20]. Nanoelectrode arrays (NEAs) constructed using vertically aligned carbon nanofibers (VACNFs) have gained much attention in recent years in the biosensing arena [21–25]. The temporal resolution and detection limit in electrochemical measurements improve with reduced size of the sensing electrodes [21,22]. Properly spaced and electrically isolated VACNFs – either regularly patterned or random on the substrate – have been studied for the ultrasensitive detection of neurotransmitters, glucose and others [23–25]. The proven ability of these nanoelectrodes can be exploited as a safer alternative to mercury electrodes in the sensitive detection of Pb^{2+} [26–28]. In the past, electron-beam lithography has typically been used to pattern these carbon nanoelectrode arrays, making the fabrication often time consuming and costly. A considerably cheaper alternative is hole-mask colloidal lithography (HCL), which also allows easy altering of electrode density [29]. We report here the first use of VACNF-based nanoelectrode arrays patterned by HCL to detect Pb^{2+} by ASV, since the toxicity of lead constitutes not only serious problems for the environment but also issues regarding human and animal health.

2. Materials and methods

Prior to use, the glassy carbon electrode (BASi) was polished with a 0.05 μm alumina slurry on a polishing cloth (catalog no. 40-7218, Buehler Co.) and washed ultrasonically in DI water for 5 min. The HCL and VACNF growth procedures for the VACNFs were followed according to previously published methods with slight modifications [29–31]. Concisely, PMMA (0.4% v/v) was dissolved in anisole for 24 h, spin coated (3000 RPM, 30 s) onto 100 nm chromium-coated silicon wafers and soft baked for 5 min (180 °C). The substrates were etched using O_2 plasma (March CS-1701 RIE) for 5 s. PolyDADMAC (0.2% aqueous solution) was drop coated and dried under N_2 gas. Then, 400 nm polystyrene spheres were drop-coated (high-density 0.16% w/v aqueous solution;

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low density 0.016% w/v aqueous) and dried under N_2 gas followed by a 5 nm gold deposition (Temescal FC-1800 E-Beam Evaporator). The substrates were tape-stripped to remove the polystyrene spheres, etched under O_2 plasma for 2 min and deposited again with 20 nm of nickel. The PolyDADMAC/PMMA templates were removed by sonicating in acetone for less than 10 s and air-dried, leaving behind patterned nickel disks with desired density and diameter.

The VACNFs were grown from 400 nm HCL-defined nickel catalyst spots in a DC-biased plasma-enhanced chemical vapor deposition reactor (BlackMagic Nanoinstruments, Cambridge UK) using ethylene feedstock (125 sccm) and ammonia etchant (444 sccm) at 700 °C, 4.7 Torr with 180 W power [30,31]. The nanofibers were encapsulated with parylene c (SCS Specialty Coating Systems) and etched for 30 s by reactive ion etching until the fiber tips buried in parylene c were re-exposed. The nanofibers were visualized using a Hitachi S-4800 field emission scanning electron microscope (Hitachi, Pleasanton, CA), operated with a 15 kV accelerating voltage.

Anodic stripping voltammetry experiments were carried out using a standard three-electrode electrochemical cell (BAS100a-electrochemical analyzer instrument and controlled by BAS100a software) containing 15 mL of solution. The counter electrode was a Pt wire, the reference electrode was an Ag/AgCl (3 M KCl) from BASi and the VACNFs acted as the working electrode. Cyclic voltammetry experiments were conducted by immersing the three electrodes into a 4-mL custom-built electrochemical cell at a scan rate of 100 mV/s. Three complete sweeps were run concurrently, the last sweep is plotted. Supporting electrolyte for all experiments was 0.1 acetate buffer (pH 4.5) [32,33]. For ASV experiments, the solutions of Pb^{2+} ranged in concentration from 48.26 nM to 482.6 nM (10 ppb to 100 ppb). Stripping analysis employs three main steps: 1. pre-concentration, 2. quiet time and 3. stripping. A deposition potential of −1000 mV was applied to the carbon nanofibers while the solution was stirred for 120 s. After a 10 s waiting period, the stripping voltammogram was recorded by applying a positive-going square wave voltammetric (SWV) potential scan (frequency of 15 Hz, amplitude of 25 mV and potential step of 4 mV). The scan was terminated at 0.0 mV. Aliquots of the target metal standard solution were introduced after the background voltammograms were recorded. A 60 s conditioning step at +500 mV was used to remove any remaining deposited Pb prior to the next cycle. All measurements were carried out at room temperature and done in triplicate.

3. Results and discussion

Prior to patterning by HCL, a thin chromium layer was used to make electrical contact with the VACNFs. The nanofibers delaminate upon perturbation unless they are encapsulated with a polymer coating; therefore, parylene c was deposited by chemical vapor deposition to improve the mechanical stability and cover the underlying chromium to minimize its interference in the electrochemical studies. Parylene c is known to produce a conformal coating on carbon nanofibers; therefore, the VACNFs were coated by parylene c by chemical vapor deposition [34,35]. The parylene was then etched with oxygen plasma to re-expose the carbon nanofibers. Scanning electron micrographs (SEM) of the VACNFs show that they are uniformly covered with a coating of parylene c (Fig. 1).

The carbon nanofiber bundles in Fig. 1 are vertically aligned and confined to the 400 nm Ni catalyst spots they were grown from. The individual fibers are approximately 80 nm in width, 2.2 μm in height and are well distributed. Two representative densities – low and high – were fabricated to elucidate the dependence of sensor performance on the fiber density. Our recent results [30] show that the surface roughness of the electrode materials can give rise to macroscopic and microscopic surface area effects. If the carbon nanofibers are in a high-density array, they are not able to act as individual electrodes because the radial diffusion layers of neighboring electrodes overlap. Conversely, if the density of the carbon nanofibers is scaled down enough, then they should operate as individual electrodes because the radial diffusion layers of adjacent electrodes will no longer overlap. Incidentally, without a pattern the density would be higher than our present high-density sample. The trend would asymptotically approach the real "forest-like" unpatterned growth. The high-density array (Fig. 1a) shows the bundling of the fibers, which is absent in the low-density array (Fig. 1b) simply because of the large space in-between the nickel catalyst spots prior to growth by PECVD. The electrode arrays fabricated by the HCL procedure are randomly ordered similar to that by Horne and Fletcher, but 8.75 times smaller in radius [36]. The exposed nanofiber density and distance to the nearest neighbor for the high-density case can be estimated from the SEM image to be ~3×10^7 CNFs/cm^2 and 1 μm, respectively. The corresponding estimates for the low-density array are ~8×10^6 CNFs/cm^2 and 3 μm, respectively.

A 0.1 M acetate buffer (pH 4.5) was used as previous works have shown its success for ASV in detecting heavy metals; SWV improves the limit of detection by reducing the interference from charging current [37]. The behavior of the fabricated electrodes was studied by CV using [Fe $(CN_6)^{3-/4-}$], which is a chemically reversible redox couple commonly used to characterize carbon electrodes because it is a robust and well characterized model system that exhibits a one-electron transfer [37,38].

Fig. 2 shows cyclic voltammograms of 2 mM [Fe $(CN_6)^{3-/4-}$] at a GC electrode, and VACNF electrode array for two different densities in an acetate buffer solution at a scan rate of 100 mV/s. Well-defined voltammetric waves are seen for the GC and high-density VACNF electrode arrays with complementary anodic and cathodic peaks. However,
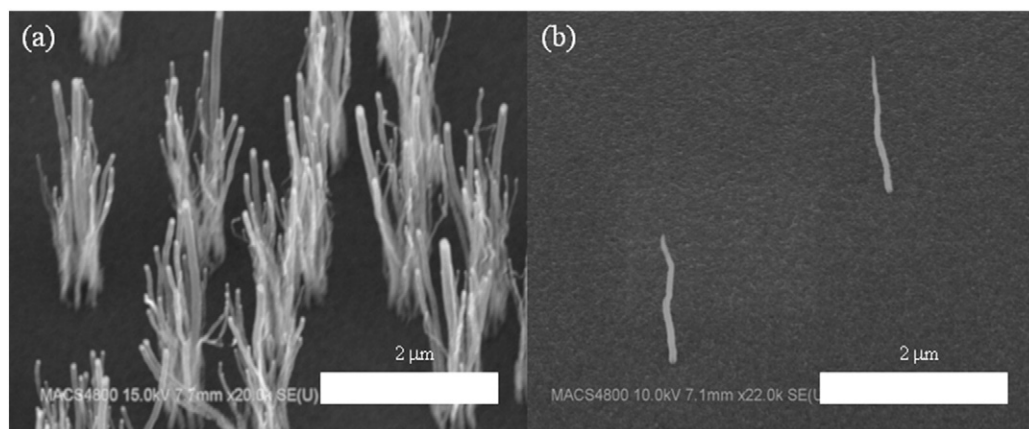

Fig. 1. Scanning electron micrographs of (a) high-density and (b) low-density nanoelectrode VACNF arrays fabricated by HCL. The nanofibers shown are after parylene c encapsulation and reactive ion etching. Scale bars 2 μm.