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Fabrication and characterization of carbon nanotube array electrodes with gold nanoparticle tips

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ABSTRACT

In this work we fabricated 8 mm long aligned multi-walled carbon nanotube array electrodes and electrochemically deposited gold nanoparticles in a controlled manner onto the nanotube tips at the top of the array. A soldering technique was also developed to provide reliable electrical contact between the carbon nanotubes at the bottom of the array and copper on a patterned printed circuit board. The top surfaces of the nanotube tower electrodes were activated using a reactive ion etcher prior to gold deposition. Electrodeposition of Au particles on the plasma-treated tower electrodes was performed over a range of deposition times and potentials. Cyclic voltammetry and electrochemical impedance spectroscopy analyses showed that the Au-deposited carbon nanotube array electrodes were successfully fabricated. The new electrodes will be the foundation for further biosensor development using self-assembled monolayers and bio-conjugation of antibodies for novel label-free immunosensing.

1. Introduction

Nanostructured electrodes using ordered arrays of carbon nanotubes (CNTs), nanobelts, and Si, ZnO, Ni, Au nanowires have shown great potential for the development of enzyme-based electrochemical biosensors and electrochemical immunosensors because they provide novel physical and electrochemical properties such as high young's modulus, conductivity, and electrocatalytic effects [1–3]. Bottom-up methods [4–8] were suggested to use these materials on the surface of an electrochemical sensor. Achieving spatial control of individual nanoparticles will improve control of the number of functional groups on the electrode surface and hence current density for the electrode. Notably, these parameters will directly influence the sensitivity achievable by an electrochemical sensor [7–12]. Furthermore, the high surface energy of nanoparticles makes them extremely reactive towards electroactive analytes. The high reactivity makes nanoparticles excellent materials for use in biological and environmental detection [12].

CNTs have attracted tremendous interest in electroanalytical chemistry because of their unique properties such as high electrical conductivity, high mechanical properties, their ability to grow on different substrates, and nanoscale-size with a high aspect ratio. Recently, the electrochemical properties of nanoelectrode arrays (NEA) based on vertically aligned CNTs were studied [11]. The use of vertically aligned CNT arrays with well-defined properties and uniform length and diameter was shown to provide unique controllability of nanotube spatial density, and conductivity, as compared to powder type CNT electrodes. These high density CNTs are often grown on catalytically patterned surfaces by chemical vapor deposition (CVD) [12–13]. Recently, studies on the CVD synthesis of single wall carbon nanotubes (SWCNT) revealed enhancement of the activity of the catalyst by adding water during the synthesis. Using this method, 2.5-mm tall single-walled CNT forests were synthesized [14].

Here, we presented a novel fabrication method for carbon nanotube array electrodes, followed by their electrochemical characterization for electroanalytical purposes. The most difficult problems faced in the electrode fabrication were achieving repeatability and low contact resistance. In this work, we report a direct soldering method of attaching the nanotube array to a pre-patterned printed circuit board (PCB) to overcome limitations in previous methods [15,16]. Further, gold was electrochemically deposited on activated end sites of the CNT array to provide better control of current density. CNTs were activated by radio frequency

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(RF) plasma treatment. Controlled density of gold on the nanotube tips was verified by cyclic voltammetry (CV) and electrochemical impedance methods.

2. Experimental

2.1. Synthesis of carbon nanotube array and device fabrication

Our group reported the synthesis of carbon nanotube arrays with specific patterns using water assisted chemical vapor deposition [14]. The synthesized CNT arrays were characterized by environmental scanning electron microscopy (ESEM). This carbon nanotube array was peeled off from the Si substrate using a pair of tweezers and placed on a copper PCB that was already patterned using photolithography. Copper boards coated with a dry photoresist film (D&L Product Inc.) were used to pattern the electrical contact between the electrode and copper. To assemble a CNT tower to PCBs, a 2–3 N pressure was applied to the CNT tower and patterned Cu contact, causing the solder to melt and contacting carbon nanotube array electrically. In this work, a eutectic alloy of 63% tin and 37% lead was used as a solder. In this way, an 8-mm long CNT tower was successfully soldered on a PCB. After cooling to room temperature, the entire assembly was immersed in epoxy. Resin 862 and EPICURE curing agent W were used to form a nanotube–epoxy composite. After casting epoxy into the array, the top section of the CNT tower was polished using a Vibromat (Buehler) polisher. The surface of the nanotube array–epoxy electrode was sequentially polished with diamond abrasive (Microid Diamond Compound) of 9, 3 and 0.5 μm with a 5-N constant force for 5 min at 150 rpm. The electrodes were then rinsed with fresh acetone spray and immediately air-dried.

In the next step of our fabrication process, gold was electrochemically deposited on the nanotube array electrodes. This initially involves an application of a reactive ion etcher (RIE) at 13.56 MHz RF plasma to remove excess epoxy on the nanotube–epoxy electrode as well as to activate the nanotube tips. The mass flow rate was set to 80 standard cubic centimeters per minutes (SCCM) with 20% oxygen and the etching was performed for 2 min at a power of 50 W. After rinsing with acetone, methanol, and H_2O, the protruding nanotube electrodes were immersed in hydrogen tetrachloroaurate solution diluted with hydrochloric acid (Aldrich) for electrodeposition of gold at an applied potential of 1.0 V (vs. Ag|AgCl) for a specific deposition times. Prior to use, the resulting gold nanoparticles was thoroughly rinsed with methanol and water and dried under a stream of nitrogen.

2.2. Electrochemical characterization

In order to evaluate the electrochemical properties of nanotube array electrodes, cyclic voltammetry and electrochemical impedance spectroscopy (EIS) were performed using a three-electrode cell consisting of a nanotube electrode as the working electrode, a Ag|AgCl reference electrode, and a platinum wire counter electrode. CV was carried out using an electrochemical analyzer (BAS, West Lafayette, IN) operated by Epsilon software with a C3 cell stand in a Faraday cage. EIS measurements were per-

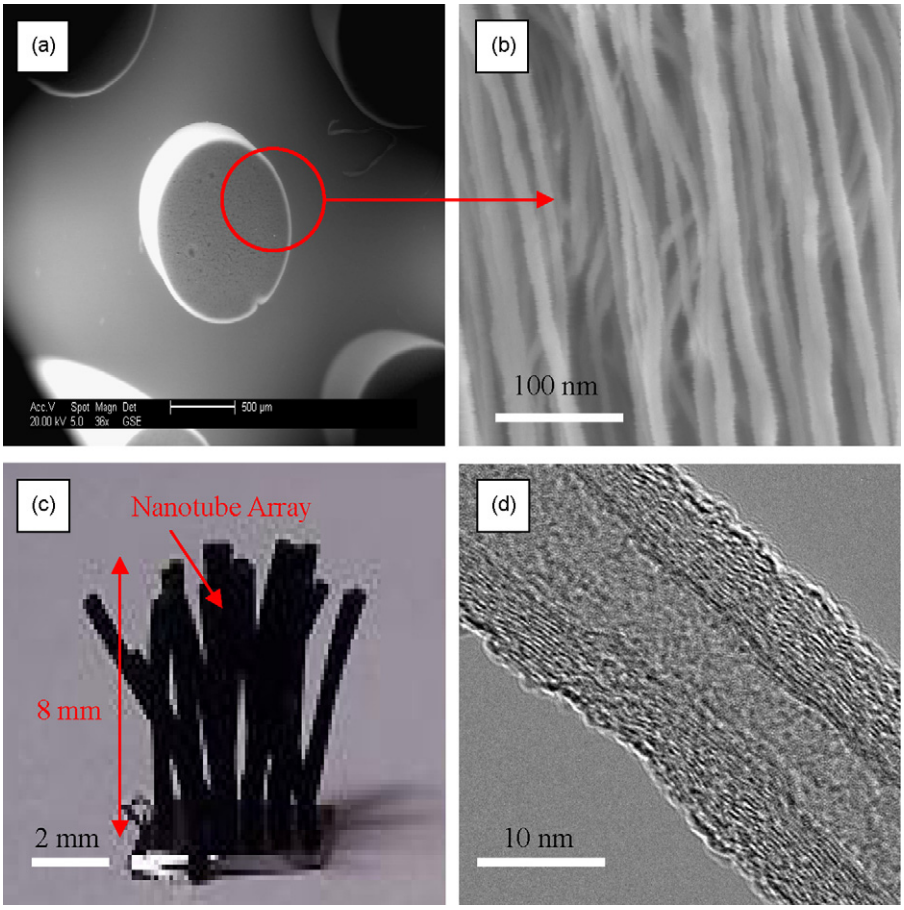

Fig. 1. ESEM images of aligned multi-wall carbon nanotube patterned arrays: (a) one bundle of nanotubes called a tower; (b) top view of nanotube tower; (c) photo of patterned MWCNT array. Growth conditions are: 200 SCCM of H_2, 200 SCCM of C_2H_4, 200 SCCM bubbler, and a 750 °C growth temperature.