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Bipolar Electrodeposition onto Carbon Nanotubes

Title: Bipolar Electrodeposition of Cadmium onto one tip of a Carbon Nanotube 1

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Abstract: The bipolar electrodeposition of cadmium onto one tip of an isolated carbon nanotube is described.

Project: Bipolar Electrodeposition onto Carbon Nanotubes

Objective: The intention of the following work is to demonstrate the use of bipolar electrochemistry to deposit cadmium onto a single tip of an isolated carbon nanotube immobilized on a polyester membrane.

Related Research:

Bipolar Electrodeposition

1. Bipolar electrochemistry refers to the anode-cathode pair on an isolated conductive substrate which is induced by an external electric field (refs 1 - 10).
2. Auxiliary electrodes (ref 1), fluidized bed electrodes (ref 2), and trace metal recovery (ref 3) are early examples of bipolar electrochemistry.
3. Previous work by Bradley et al includes the use of spatially coupled bipolar electrochemistry (SCBE) to grow silver nanowires (ref 4) and micron size copper wires from isolated copper beads (ref 5).
4. The synthesis of a bipolar electrodeposited catalyst has been studied (ref 6).
5. Cobalt (ref 7), nickel (ref 8), tin (ref 9), and polypyrrole (ref 10) have also been electrodeposited onto carbon nanotubes (CNTs) using bipolar electrodeposition.

Electrodeposition onto Carbon Nanotubes

1. Copper has been electrodeposited onto multi-walled carbon nanotubes (MWCNTs) in order to study the electrochemical behavior of the MWCNTs (ref

11).

2. The electrode nanotube contact resistance in a carbon nanotube field-effect transistor was studied by electroplating gold onto single-walled carbon nanotubes (SWCNTs) deposited across two prefabricated electrodes. This method required direct contact to the nanotubes and lithography (ref 12).
3. SWCNTs were chemically bonded to a gold substrate and copper was deposited by conventional electrochemical methods onto the SWCNTs. Microelectrode arrays were demonstrated with potential applications in electrochemical sensors and nanowire array fabrication (ref 13).
4. MWCNTs were coated with polypyrrole using electrochemical polymerization. Suggested applications for the resulting nanotube polymer composites include super capacitors, secondary batteries, and sensors (ref 14).
5. Co-deposition of MWCNTs and nickel using electrodeposition techniques to produce a metal MWCNT composite were presented (ref 15).

Electrodeposition of Cadmium onto Carbon

1. Cadmium was electrodeposited onto vitreous carbon and tin oxide electrodes in order to study the nature of cadmium electrodeposition from various aqueous systems (ref 16).
2. Cadmium was electrodeposited from aqueous solution onto freshly cleaved graphite as a first step in the synthesis of cadmium sulfide quantum dots (ref 17).

Experimental Description: A 1.0 mL sample of a 0.1 microgram/mL suspension of commercial MWCNTs (NanoLab Inc, 50 nm nominal diameter, 10 micrometer nominal length) in HPLC grade tetrahydrofuran was obtained. This was filtered through a 13 mm nuclear track etched polyester membrane (Osmonics Laboratory Products, 200 nm pore size). A strip, approximately 5 mm wide x 10 mm, was cut out of the center of the membrane and was set up in an experimental cell (figure 1). The experimental cell was placed in a beaker and set up for electric field application. A 50 mL solution consisting of 1.0 mM cadmium chloride in 20% dimethyl sulfoxide (DMSO) and 80% toluene was added. The DMSO had been dried over calcium hydride and then distilled under reduced pressure. The toluene had also been dried over calcium hydride. A pulsed DC electric field was applied with an on-time of 1.0 millisecond, an off-time of 24.0 milliseconds, and a field intensity of 10 kV/cm. The total on-time was 60 seconds. The electric field was controlled using a high voltage switch (Behlke HTS 651-03-LC) controlled by an HP33120A function generator. After the field application, the cell was placed in 100 mL of HPLC grade DMSO for 5 minutes to wash away excess reagents. The membrane strip was placed in a glass vial, and the nanotubes were re-suspended by adding 0.5 mL of acetone. A 1 mL syringe was used to repeatedly pump the acetone over the membrane. The suspension was then drop-dried onto the polished side of a 3 mm x 3 mm piece of silicon wafer. The wafer was mounted on an SEM stub and then examined on a Phillips XL-30 field emission scanning electron microscope (SEM).

Results: Figure 2 shows an isolated CNT with cadmium deposit on one tip. The total length of the nanotube from the uncoated tip to the end of the deposit is approximately 9 microns. The total length of the cadmium deposit is approximately 5 microns, and it covers over half the length of the nanotube. In figure 3, the isolated CNT has an approximate length of 6 microns, with the deposit extending down to the center of the nanotube for an overall length of 3 microns. In both images, the deposit is only on one tip of the nanotube.

Discussion :

- The potential difference across the tips of a CNT in an electric field can be estimated by taking the product of the length of the nanotube and the electric field (ref 6).
- In figure 2, the potential difference across the CNT is approximately 9.0 V (10 kV/cm x 9.0 microns). In figure 3, the potential difference is approximately 6.0 V (10 kV/cm x 6.0 microns). These values are well above the reduction potential of cadmium in aqueous solution (refs 16, 17).
- Inside the electric field, each CNT forms an anode-cathode pair. Thus, cadmium will electrodeposit onto one tip only, i.e. the cathode (refs 2, 6).
- At 10 kV/cm, the minimum length of a CNT for the bipolar electrodeposition of cadmium is 300 nm. In addition, the potential at the center point of the CNT will be zero, and as a result, no cadmium metal will nucleate and grow at or near the center of the CNT. However, figures 2 and 3 have cadmium deposition that extends over 50% of the total length of the structures. One possible reason is that the overall lengths of the CNTs cannot be determined from the images because the cadmium deposits are too thick, and they obscure the tips of the CNTs. Without being able to determine the true lengths of the CNTs, the true percentages of the CNTs that are covered by the deposits cannot be determined. Thus, it is more likely that the cadmium deposits have grown off the tips of the nanotubes as short nanowires.

Conclusions: Bipolar electrochemistry was successfully used to electrodeposit cadmium onto one tip of an isolated CNT. The conditions used were a 10 kV/cm pulsed (on-time: 1 millisecond, off-time: 24 milliseconds) DC electric field, and a solution of 1.0 mM cadmium (II) chloride in dry DMSO and dry toluene (1 DMSO: 4 toluene).

Figure 1:

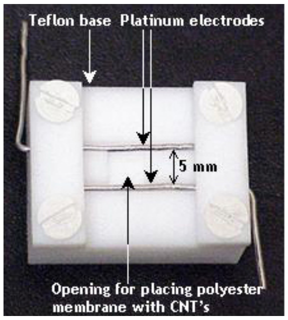


Figure 2:

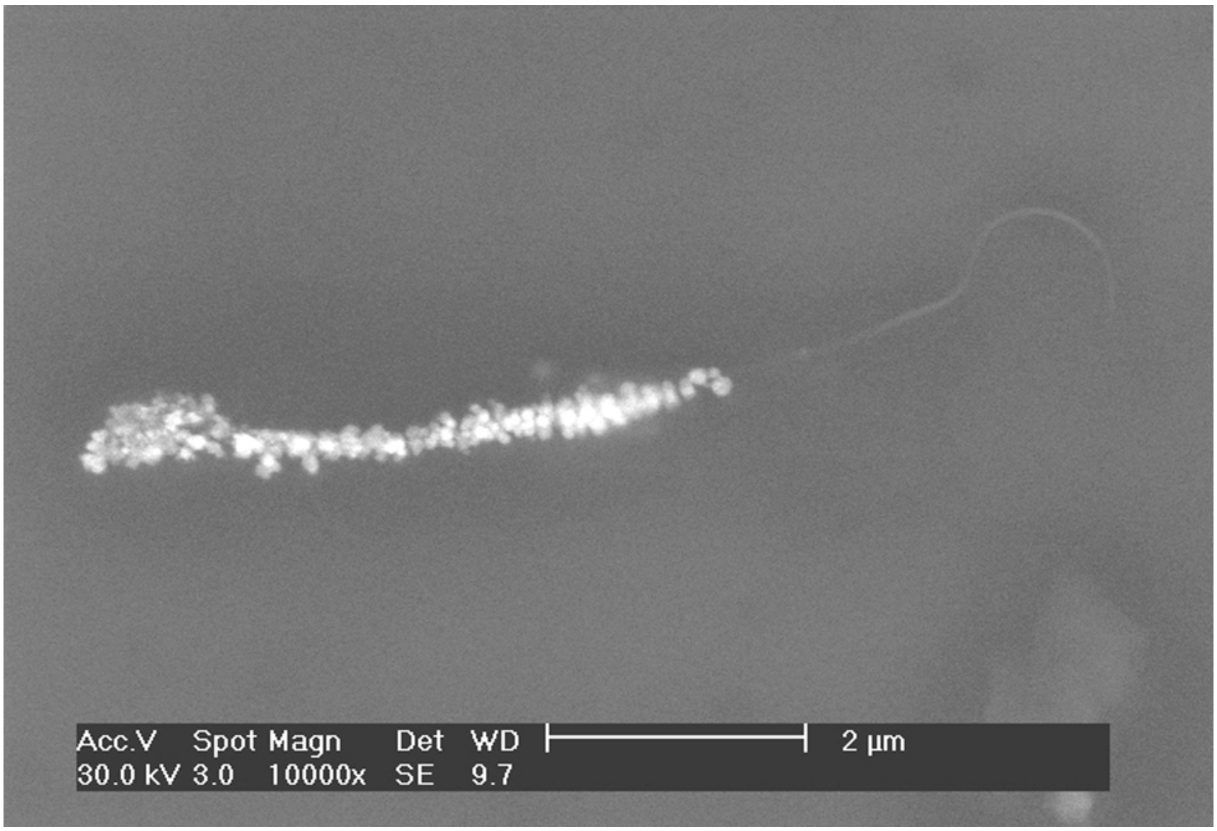
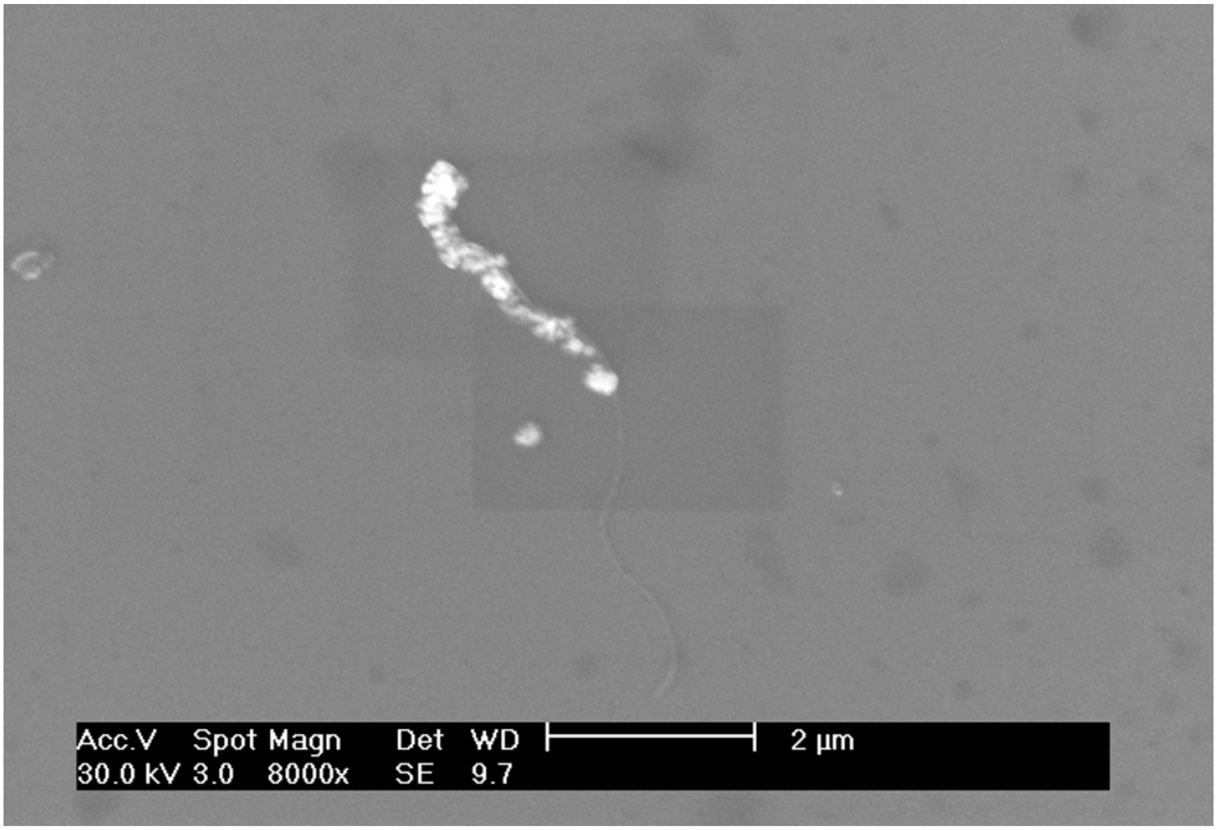


Figure 3:



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