NANO LETTERS

2003
Vol. 3, No. 1
107−109

Nanoelectrode Arrays Based on Low Site Density Aligned Carbon Nanotubes

Y. Tu

Department of Chemistry, Boston College, Chestnut Hill, Massachusetts 02467

Yuehe Lin

Pacific Northwest National Laboratory, 902 Battelle Boulevard, Richland, Washington 99352

Z. F. Ren*

Department of Physics, Boston College, Chestnut Hill, Massachusetts 02467

Received November 5, 2002; Revised Manuscript Received November 22, 2002

ABSTRACT

Nanoelectrode arrays (NEAs) were fabricated from low site density aligned carbon nanotubes (CNTs). The CNTs were grown by plasma-enhanced chemical vapor deposition on Ni nanoparticles made by electrochemical deposition. Each nanotube is separated from the nearest neighbor by several micrometers. NEAs of 1 cm^2 consisting of up to millions of individual nanoelectrodes, each with a diameter of 100 nm, were made by this nonlithography method. These carbon NEAs could be used as templates to fabricate other metal NEAs. Electrochemical characterization including cyclic voltammetry and square wave voltammetry were performed.

Ultramicroelectrode arrays (UMEAs) consisting of hundreds of metal UMEs with diameters of several micrometers[1,2] have been fabricated by lithographic techniques. The UMEAs show many advantages over the conventional macroelectrodes such as high mass sensitivity, increased mass transport, and a decreased influence of the solution resistance. Further size reductions of each individual electrode to nanometers and an increase in the total number of electrodes can improve the detection limits and the signal-to-noise (S/N) ratio since the noise level depends on the active area of the individual electrode whereas the signal depends on the total area of the electrodes.[3,4]

Carbon electrodes have a wide useful potential range, particularly in the positive direction, due to the slow kinetics of carbon oxidation. Besides, carbon is a versatile electrode material that can undergo various chemical and electrochemical modifications to produce flexible surfaces to influence reactivity. Carbon nanotube (CNT) electrodes[5] could be of great significance in both fundamental and applied electrochemistry because of their unique properties such as a high aspect ratio and good electrical conductivity. Vertically aligned CNTs[6] have good material properties and are of the right size (20 to 200 nm) to be nanoelectrode arrays (NEAs),[7] but they do not have the right spacing, which needs to be sufficiently larger than the diameter of the nanotube, to make each nanotube work as an individual nanoelectrode.[8] Electron-beam (e-beam) lithography had been used to control the site density of the CNTs,[9] and several individually addressable CNTs based on an electrochemical probe array have been fabricated.[10] However, e-beam lithography is not suitable for commercial scale-up.

Recently, we successfully controlled the site density of aligned CNT arrays by creating a controllable site density of Ni nanoparticles using electrochemical deposition.[11] Low site density aligned CNT arrays with an interspacing of more than several micrometers were achieved by this nonlithography method. In this paper, we reported the fabrication of NEAs consisting of up to millions of nanoelectrodes from these low site density CNT arrays with each electrode 100 nm in diameter.

The growth of low site density aligned CNT arrays has been reported previously.[11] Briefly, Ni nanoparticles were randomly electrodeposited on a 1-cm^2 Cr-coated silicon substrate by applying a pulse current to the substrate in $NiSO_4$ electrolyte solution. The size and the site density of the Ni nanoparticles were controlled by the amplitude and the duration of the pulse current. CNT growth was performed in the plasma-enhanced chemical vapor deposition (PECVD) system at 650 °C for 8 min with 160 sccm NH_3 and 40 sccm C_2H_2 gases with a total pressure of 15 Torr and a plasma intensity of 170 W. The CNTs are about 8 μm in length and

* Corresponding author. E-mail: renzh@bc.edu.

10.1021/nl025879q CCC: $25.00 © 2003 American Chemical Society
Published on Web 12/12/2002

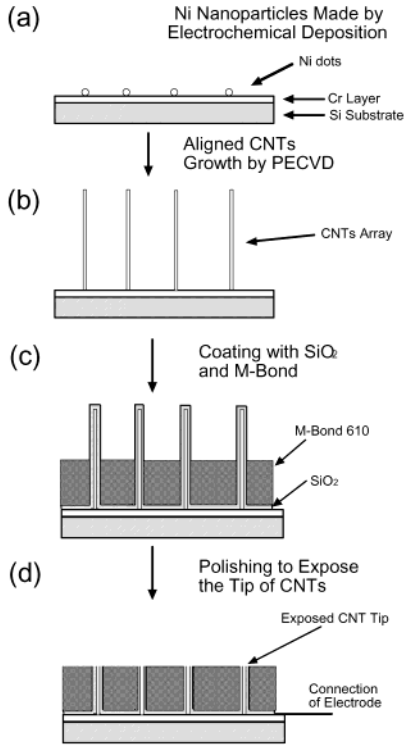

Figure 1. Fabrication scheme of the NEAs. (a) Ni nanoparticles electrodeposition; (b) aligned carbon nanotube growth; (c) coating of SiO_2 and M-Bond; and (d) polishing to expose CNTs.

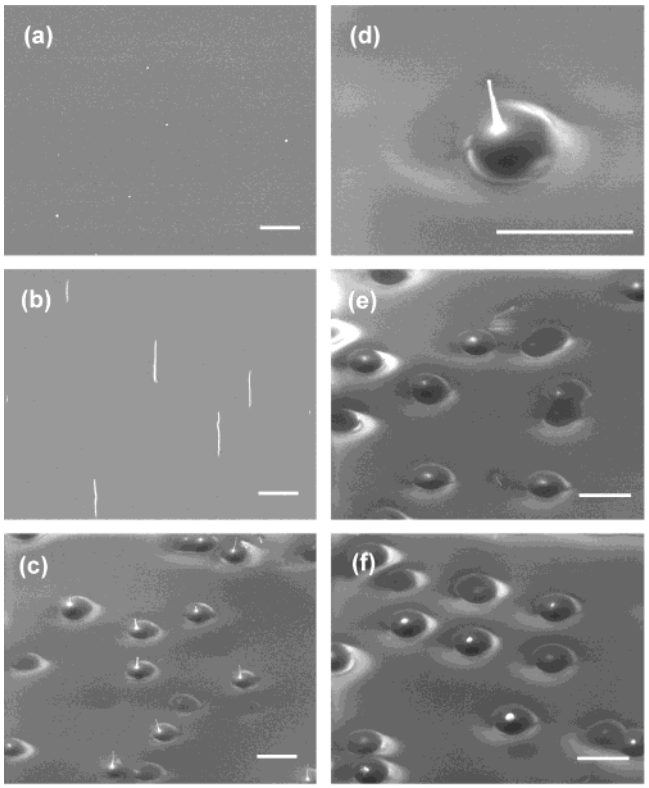

Figure 2. Scanning electron microscope images. (a) Top view; (b−f) from a 45° side view. All of the scale bars represent 5 μm. (a) Electrodeposited Ni nanoparticles; (b) low site density aligned CNTs array; (c) CNTs array coated with SiO_2 and an epoxy layer, (d) close-up look at a single half-embedded CNT; (e) CNTs after polishing; and (f) second electrodeposition of Ni nanoparticles on the broken CNTs only.

100 nm in diameter. The average spacing between nanotubes is about 10 μm, which corresponds to a site density of 10^6 per cm^2.

Figure 1 shows the scheme of the fabrication procedure. After the electrochemical deposition of Ni nanoparticles (shown in 1a), an aligned CNTs array was grown (shown in 1b), and then a thin layer of SiO_2 was coated on the surface by magnetron sputtering to insulate the Cr layer. After that, 5-μm-thick M-Bond 610 (two-component, solvent-thinned, epoxy-phenolic adhesive from Vishay Intertechnology, Inc.) was coated and cured at 170 °C for 2 h, which further insulates the Cr and also provides mechanical support to the CNTs. After these steps, the CNTs were half embedded in the polymer resin as shown in Figure 1c. In the next step, a fiber-free cloth was used to polish the surface that mechanically breaks the top part of the CNTs and exposes the tip of the CNTs as shown in Figure 1d. Finally, the sample surface was rinsed in deionized water, and an insulated copper wire (0.5 mm in radius) was attached to the corner of the substrate by applying a drop of conductive silver epoxy followed by insulating epoxy. The copper wire−NEAs assembly was left to cure in air at room temperature for several hours.

Figure 2 shows the SEM images of the NEA fabrication steps corresponding to the scheme shown in Figure 1. The bright dots in Figure 2a are the electrodeposited Ni nanoparticles that are randomly distributed on the substrate. This sample has a site density of about $10^6/cm^2$ and an average interspacing of about 10 μm. Figure 2b shows the low site density aligned CNTs array grown by the PECVD method from the Ni nanoparticles. Figure 2c shows the morphology after coating with a thin layer of SiO_2 followed by a second layer of epoxy film. The CNTs arrays were half embedded in the polymer. Figure 2d provides a close-up look at a single half-embedded CNT. Figure 2e shows the topography after polishing. It is clearly shown that only the tips of the embedded CNTs were exposed. To prove that the tip of the CNTs is exposed and conducting, we repeated the electrodeposition of the Ni nanoparticles on the sample. Figure 2f shows that the Ni nanoparticles were deposited only on the CNTs' tips, not elsewhere. This also indicates that the carbon NEAs array could be used as a template to fabricate other metal NEAs.

Electrochemical characterization was performed with a CHI 660 electrochemical analyzer (CH Instruments, Austin, TX). A one-compartment cell was used with a platinum wire as the auxiliary electrode and Ag/AgCl as the reference electrode. The cyclic voltammetry of $K_3Fe(CN)_6$ was used for the characterization of the NEAs. As shown in Figure 3, the relative heights of the anodic and cathodic peaks in the cyclic voltammograms indicated the reversibility of the electrochemical reaction of the $Fe(CN)_6^{4-}/Fe(CN)_6^{3-}$ redox couple on native carbon NEAs. The difference between forward and reverse scans deviated from the sigmoid shape expected from the microelectrode. This may be due to the partial overlapping of the diffusion layers of individual nanoelectrodes or to leakage due to the insufficient passive layer. In addition, the surface condition of the electrode and

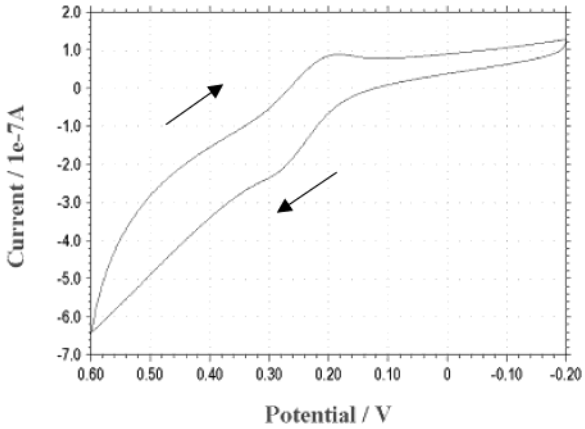

Figure 3. Cyclic voltammetry curve of the carbon NEAs. The curve was taken in a solution of 4 mM $K_3Fe(CN)_6$ in 0.5 M KNO_3. The scan rate was 40 mV/s.

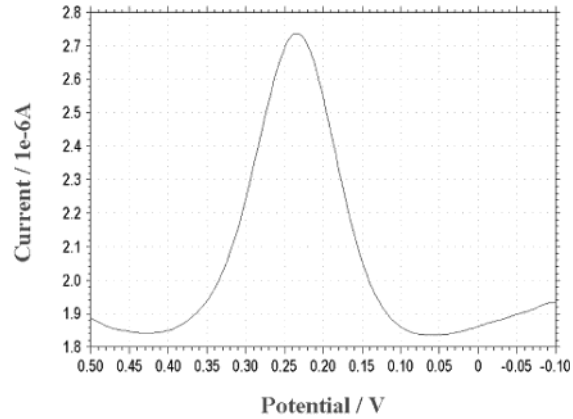

Figure 4. Square wave voltammetry data of the carbon NEAs. The curve was taken in solution of 2 mM $K_3Fe(CN)_6$ in 0.5 M KNO_3. Pulse amplitude, 25 V; step amplitude, 4 mV; frequency, 15 Hz.

the scan rate could also affect the results. More experiments are under way to improve the performance of the NEAs. The signal (in the range of microamperes) generated from the NEAs fabricated here is much higher compared with the signal (a few picoamperes) generated from a couple of carbon nanoelectrodes with a similar disk shape [10] simply because the total current for the loosely packed electrode array is proportional to the number of individual electrodes: $i_{array} = Ni_{single}$.[8] This will avoid the need for expensive electronic device for low-current detection.

Square wave voltammetry (SWV) is a powerful technique for electroanalysis. SWV is a large-amplitude differential technique in which a waveform composed of a symmetrical square wave, superimposed on a base staircase potential, is applied to the working electrode.[12] The main advantages of SWV are speed and low detection limits. SWV can effectively discriminate the signal against the charging background current, enabling very low detection limits for the analytes. To evaluate the potential applicability of the carbon NEAs for trace analysis, SWV of $K_3Fe(CN)_6$ was studied. As shown in Figure 4, a symmetric peak of $K_3Fe(CN)_6$ reduction was obtained, which indicated that the carbon NEAs are promising for analytical purposes such as metal ion detection in environmental analysis and as biosensors. Compared with the CV curve in Figure 3, the charging background current in the SWV curve was dramatically reduced.

In summary, carbon NEAs consisting up to millions of nanoelectrodes have been fabricated by a nonlithography method. It can also be used as a template to fabricate other metal NEAs. Cyclic voltammetry and square wave voltammetry were used to characterize the carbon NEAs. Detailed electrochemical characterization and application of these carbon NEAs are currently being explored in our lab, and the results will be reported subsequently.

Acknowledgment. This work performed at Boston College is supported partly by DOE under a grant DE-FG02-00ER45805, partly by NIH under grant NIH CA-97945-01, partly by the US army Natick Soldier Systems Center under grants DAAD16-02-C-0037 and DAAD16-00-C-9227, and partly by NSF under a grant ECS-0103012. The work performed at Pacific Northwest National Laboratory (PNNL) is supported by a LDRD program at PNNL. PNNL is operated by Battelle for the U.S. Department of Energy (DOE). The work was partially performed at the Environmental Molecular Sciences Laboratory, a national scientific user facility sponsored by the U.S. DOE's Office of Biological and Environmental Research, located at PNNL.

References

(1) Feeney, R.; Kounaves, S. P. *Electroanalysis* **2000**, *12*, 677.
(2) Henry, C. S.; Fritsch, I. *Anal. Chem.* **1999**, *71*, 550.
(3) Menon, V. P.; Martin C. R. *Anal. Chem.* **1995**, *67*, 1920.
(4) Weber, S. G. *Anal. Chem.* **1989**, *61*, 295.
(5) Campbell, J. K.; Sun, L.; Crooks, R. M. *J. Am. Chem. Soc.* **1999**, *121*, 3779.
(6) Ren, Z. F.; Huang, Z. P.; Xu, J. W.; Wang, J. H.; Bush, P.; Siegal, M. P.; Provencio, P. N. *Science (Washington, D.C.)* **1998**, *282*, 1105.
(7) Chen, J. H.; Huang, Z. P.; Wang, D. Z.; Wen, J. G.; Ren, Z. F. *Electrochem. Soc., Proc.* **2001**, *11*, 362.
(8) Morf, W. E.; de Rooij, N. F. *Sens. Actuators, B* **1997**, *44*, 538.
(9) Ren, Z. F.; Huang, Z. P.; Wang, D. Z.; Wen, J. G.; Xu, J. W.; Wang, J. H.; Calvet, L. E.; Chen, J.; Klemic, J. F.; Reed, M. A. *Appl. Phys. Lett.* **1999**, *75*, 1086.
(10) Guillorn, M. A.; McKnight, T. E.; Melechko, A.; Merkulov, V. I.; Britt, P. F.; Austin, D. W.; Lowndes, D. H.; Simpson, M. L. *J. Appl. Phys.* **2002**, *91*, 3824.
(11) Tu, Y.; Huang, Z. P.; Wang, D. Z.; Wen, J. G.; Ren, Z. F. *Appl. Phys. Lett.* **2002**, *80*, 4018.
(12) Osteryoung, J.; Osteryoung, R. A. *Anal. Chem.* **1985**, *57*, 101A.

NL025879Q