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Ultrahigh-Surface-Area Metallic Electrodes by Templated Electroless Deposition on Functionalized Carbon Nanofiber Scaffolds

Kevin M. Metz, Kiu-Yuen Tse, Sarah E. Baker,
Elizabeth C. Landis, and Robert J. Hamers*

*Department of Chemistry, University of Wisconsin−Madison,
1101 University Avenue, Madison, Wisconsin 53706*

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The recent emphasis on solving materials issues associated with fuel cells, supercapacitors, and other emerging technologies for storage and conversion of energy is leading to great interest in high-surface-area materials and nanocomposites.[1−5] Nanoscale forms of carbon such as nanotubes and nanofibers are intriguing because in addition to providing high surface areas, excellent thermal stability, and good electrical conductivity,[2,6] they can be combined with metal nanoparticles and other materials to form composite structures with tailored electrical and chemical properties.[3−7] Composites based on vertically aligned carbon nanofibers (VACNFs)[8,9] are particularly interesting for applications such as electrocatalysis and fuel cells because VACNFs prepared using the methods employed here form in a stacked-cup arrangement that exposes edge-plane graphite along the sidewalls,[9] leading to increased electrical and chemical activity.[10] Because carbon has a low reactivity,[11] both electrochemical and electroless deposition of metals onto nanofibers and other forms of carbon typically requires an activation process in which harsh oxidizing acids are used to produce carboxylic acid sites on the surface.[3,12,13] However, these treatments are often incompatible with metal electrode structures made using common metals.[3,5,13]

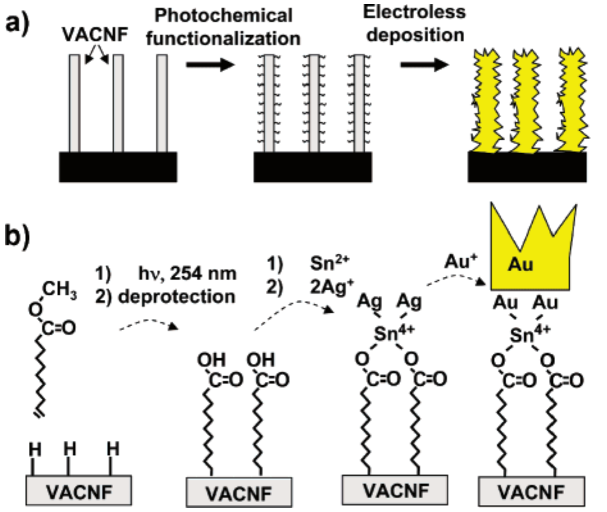

Figure 1. (a) Schematic illustration of the steps involved in the functionalization of carbon nanofibers and subsequent proceudure for electroless deposition. (b) Chemical transformations involved in the nanofiber modification.

Here, we demonstrate a method for producing nanostructured metal electrodes by functionalizing carbon nanofibers with molecular layers bearing carboxylic acid groups, which then serve as a template for electroless deposition of gold. Functionalization of the nanofibers with an organic monolayer exposes carboxylic acid groups under mild conditions. These carboxylic acids yield very high nucleation densities during electroless deposition, producing high densities of nanocrystals that evolve into a continuous film of highly nanotextured gold, completely coating the carbon nanofibers. Our method results in ultrahigh-density, high-effective-surface-area materials whose interfacial capacitance exceeds that of a planar gold electrode by nearly 2 orders of magnitude and exceeds that of the VACNF templates by 1 order of magnitude.

Vertically aligned carbon nanofibers were grown in a custom-built DC plasma-enhanced chemical vapor deposition (DC-PECVD) chamber, using a Ni catalyst using acetylene and ammonia feed gases.[14] Typical growth conditions yield high densities of cylindrical, vertically aligned fibers, with an average diameter of ∼80 nm. Nanofibers used here were grown for 15 min, which yields length of ∼2 μm. Transmission electron microscopy images (not shown) reveal that the nanofibers adopt a stacked-cup arragement in which graphene sheets make an angle of ∼8° with respect to the fiber axis, leading to exposed graphite edge planes every 2−3 nm along the sidewalls.[15]

Figure 1 shows a schematic representation of the procedure used, which is described in detail in the Supporting Informa-

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* Corresponding author. E-mail: hamers@chem.wisc.edu. Phone: (608) 262-6371. Fax: (608) 262-0453.

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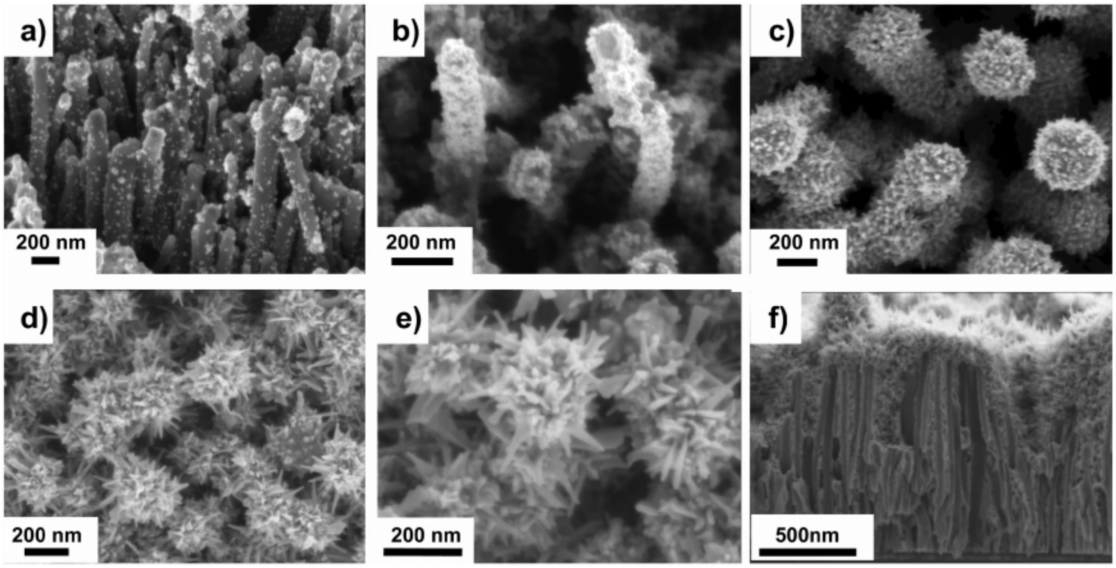

Figure 2. SEM images of gold-coated VACNFs after various times in the gold electroless deposition bath: (a) 1, (b) 3, (c) 5, (d) 7.5, (e) 7.5, and (f) 22 h.

tion. The electroless deposition method used here requires a carboxylic acid terminated surface as a starting point.[16] A key aspect of our method is to create a very high density of carboxylic acid sites on the nanofiber sufaces. We achieve this using a recently developed strategy for functionalization of carbon-based materials[17] in which nanofibers will covalently link to molecules bearing an alkene (C═C) group upon illumination with ultraviolet light at 254 nm. We reacted nanofibers with the methyl ester of undecylenic acid using 254 nm light for 16−18 h and then converted the methyl ester groups to carboxylic acids, yielding carbon nanofibers functionalized with carboxylic acid moieties. We recently showed that this procedure forms self-terminating molecular layers that still permit facile electron transfer,[18] so that the monolayer does not adversely impact the electrical contact between the nanofibers and the deposited gold layers.

Electroless deposition[16,19] was achieved by immersing the carboxylic acid-modified nanofibers in a tin-sensitizing solution and then activating it with silver. This leaves neutral atomic silver (Ag_0) bound to the surface.[16] Finally, the samples were placed in individual electroless deposition baths at 6 °C for durations of 1−22 h.

Figure 2 shows scanning electron microscope (SEM) images of the nanofiber samples after various immersion times in the gold bath. After 1 h (Figure 2a), small gold clusters are visible. After 3 h (Figure 2b), additional nuclei appear and some particles have begun to grow together. After 5 h (Figure 2c), they appear to be fully coalesced, forming a gold sheath that encapsulates each nanofiber, with protruding spikes up to 50 nm long. Upon continued immersion, the surface develops an even finer nanoscale texture. Images d and e of Figure 2 show a sample after 7.5 h, exhibiting spikes up to 100 nm long. After 11 h (not shown), the microstructure features are ∼200 nm long, and features from neighboring fibers begin to touch. Finally, after 22 h in the gold bath, the microstructure of the gold is highly textured, with spikes up to 400 nm long. Cross-sectional images after 22 h (Figure 2f) show that the space between neighboring fibers becomes filled in with a network of spikelike structures, forming a porous network. The spikelike structures were not observed in control experiments using identically prepared samples samples of amorphous carbon.

Additional control experiments were performed in which we compared the metal deposition on “bare” nanofibers and on nanofibers functionalized with the molecules carboxylic acid groups. In both cases, all other other steps were identical. The resulting SEM images, included in the Supporting Information, show that the nanofibers that were covalently functionalized exhibit a much higher nucleation density and growth rate of gold on their surfaces. We attribute this difference to the high density of surface carboxylic acid groups provided by the molecular functionalization route.

One key factor controlling the practical utilization of high surface-area electrodes is the extent to which the surface area is electrochemically accessible. To evaluate this, we used electrochemical impedance spectroscopy (EIS)[20] to measure the real (Z') and imaginary (Z'') parts of the complex impedance at the open circuit potential in a 0.1 M KCl solution using an Ag/AgCl reference electrode. We then extracted the interfacial capacitance as a function of frequency f using the equation[20]

$$C = \frac{-1}{2\pi f Z''}$$

Figure 3a shows the capacitance vs frequency for the 7.5 h sample up to 1 kHz, normalized by the sample area. For comparison, the graph also shows similar data measured on bare carbon nanofibers and a gold planar electrode. The gold-coated nanofibers show a very high capacitance, exceeding

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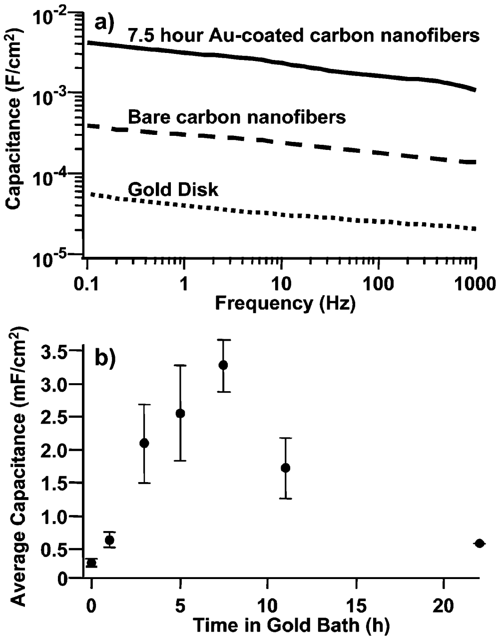

Figure 3. (a) Frequency-dependent capacitance of gold-coated carbon nanofibers, bare carbon nanofibers, and planar gold samples. (b) Effective capacitance of Au-coated VACNFs as a function of electroless deposition time.

0.04 F/cm^2 at 0.1 Hz. Because the observed capacitance is frequency-dependent, a more convenient way to compare samples is to use an effective capacitance C_{eff} by fitting the complex impedance data to an equivalent circuit consisting of a resistor and capacitor in series. Fitting data for the Au-coated nanofibers yields $C_{\mathrm{eff}} = 3.25$ mF/cm^2. That value is nearly 100 times higher than the value of $C_{\mathrm{eff}} = 33.2$ μF/cm^2 obtained on the planar gold electrode. Even more striking is that it is more than 10 times larger than the ~290 μF/cm^2 observed on the bare carbon nanofiber that serves as a template for the gold deposition. Because all measurements were performed in the same solution, these differences in capacitance reflect differences in electrically accessible surface area of the three materials.

Figure 3b shows C_{eff} as a function of time in the gold bath. C_{eff} increases rapidly, reaching a maximum of 3.25 mF/cm^2 after 7.5 h before beginning to decrease again. The decrease in $\mathrm{C}_{\mathrm{eff}}$ at longer times can be explained by a loss in accessible surface area of the electrode. As the space between adjacent fibers fills in, at long deposition times, the surface area along the lengths of the carbon fibers becomes inaccessible. Eventually, only the topmost layer of gold is accessible, leading to a decrease in the capacitance.

The high surface area of these electrodes provides capacitance values similar to those observed in bulk porous gold electrodes formed by selective leaching of one component of a metallic alloy.[21] Although the detailed mechanism underlying the complex growth strucures is not yet understood, our experiments suggest that there are two key factors. First is the high nucleation density that is provided by the molecular functionalization layer. Previous studies of metal deposition onto nanofibers have typically used harsh chemical oxidizers such as nitric acid or sulfuric acid.[3,5,13] However, these produce nanofibers with a mixture of oxidized species, only some of which are effective at binding metals.[5] By using a molecular functionalization layer, we achieve a high density of carboxylic acid groups using processing methods that are completely compatible with underlying metal electrodes. The second key factor is the use of electroless deposition rather than electrochemical deposition. Electroless deposition, especially at low temperatures, leads to complete coverage of the nanofiber sidewalls.

Although not visible in Figure 2, the gold deposits also reduce the clumping of nanofibers that is often observed after wetting and drying. Clumping reduces the accessible surface area.[14] Whereas nanofibers having only small amounts of deposited gold (as in images a and b of Figure 2) still exhibit clumping (not shown), the nanofibers with spiked structures (as in Figure 2d) show no evidence for clumping after wetting and drying, thereby enhancing their utility in aqueous environments.

Although carbon nanofibers provide a high-surface-area substrate, our work demonstrates a method for fabricating complex nanoscale structures exhibiting 10 times higher electrically active surface area than the nanofiber template, and 100 times higher than a planar surface. The very high, electrically accessible surface area, tunable gold coverage, and possibility of using a similar process for other metal electrodes suggests that the procedures outlined here may be useful for preparing a wide range of nanostructured matallic nanocomposites with novel electrical, catalytic, and/or electrocatalytic properties.

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Supporting Information Available: Complete desciption of procedures for functionalization and electroless deposition. Scanning electron microscope images of gold deposition on covalently functionalized nanofibers and control experiments on “bare” nanofibers (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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