Communications to the Editor

Electrochemistry Using Single Carbon Nanotubes

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We report here the fabrication and characterization of electrodes constructed from single carbon nanotubes. The sigmoidal voltammetric response of these nanotubular electrodes is characteristic of steady-state radial diffusion. The limiting current of uninsulated electrodes scales linearly with the depth of immersion into electrolyte solutions. However, the walls of nanotubular electrotrodes can be selectively insulated with a thin layer of polyphenol so that electrochemical activity is limited to the tip region. In this case the limiting current is essentially independent of immersion depth. These nanotubular electrodes are robust, can be fabricated in high yield, and are of uniform diameter. Most importantly, their great strength and high length-to-diameter aspect ratio will be particularly valuable for applications such as scanning electrochemical microscopy (SECM)[1,2] and electrochemical analysis of biological materials.[3−6]

Interest in carbon nanotubes stems from their unique geometrical, mechanical, electronic, and chemical properties.[7,8] To date, most fundamental research on nanotubes has been focused on their growth mechanism,[9] their sorption properties,[10] refinement of production and purification methods,[11−13] and direct measurements of various physical properties.[14−18] Practical applications

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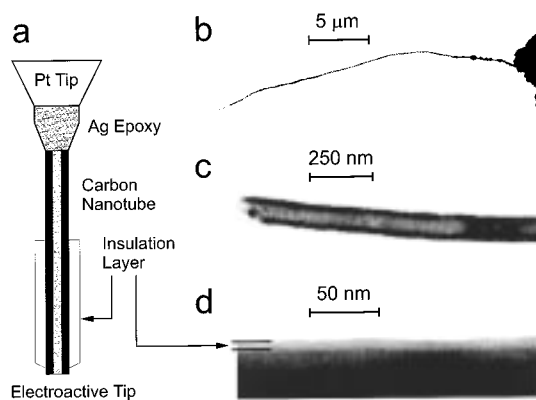

Figure 1. (a) Schematic representation of a partially insulated carbon-nanotube electrode. (b−d) TEM images of mounted nanotubular electrodes showing (b) a 30-μm long electrode; (c) the tip of a ∼100-nm diameter uninsulated nanoelectrode; (d) a ∼10-nm thick insulation layer of polyphenol on a ∼220-nm diameter nanotube.

have also been considered[19−21] but have so far been limited to their use as tips in scanning probe microscopy (SPM).[22,23]

To make practical electrochemical probes, nanotubes must be attached to and in ohmic contact with a macroscopic, conductive handle and cut to the desired length. Additionally, for many electrochemical applications, the nanotube walls must be insulated. Figure 1 shows a schematic illustration of an insulated nanoelectrode and transmission electron microscopy (TEM) images of several electrodes that reveal details about the electrode microstructure.[24] The electrodes consist of 80−200 nm diameter carbon nanotubes attached to sharpened Pt wires and cut to a length of 15−50 μm (part b of Figure 1).[25] Part c of Figure 1 shows a high-resolution image of the end of a clean nanotube, and part d shows the side of a nanotube after being electrically insulated with polyphenol by cycling the potential of the nanotube between 0 and 1.0 V (vs an Ag/AgO wire) in a pH 0.3 aqueous phenol solution for 30 min. The insulation at the tip of the nanotube can be removed either by applying a −1.0 V bias with the tip immersed in aqueous 0.1 M K_2SO_4 or by applying a voltage in air between the free end of the nanotube and a point along its side, which cuts the nanotube and exposes a fresh uninsulated tip.

Figure 2 shows cyclic voltammograms (CVs) of aqueous 5 mM $Ru(NH_3)_6^{3+}$ obtained at an uninsulated 150-nm diameter nano-

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(24) Carbon nanotubes, produced via a chemical vapor deposition process (Alig, R. L.; Burton, D. J. Carbon '97, 23rd Biennial Conference on Carbon, July, 1997), consist of a graphitic tube coated with amorphous carbon. Typically, the inside diameter ranges from 50 to 100 nm; the outside diameter from 100 to 200 nm; and the length from 100 to 500 μm.

(25) To construct nanoelectrodes, single nanotubes were attached to a mechanically cut Pt tip using Ag epoxy (Epoxy Technology Inc.) and subsequently cleaned by immersion in a fresh piranha solution (3:1 concentrated H_2SO_4:30% H_2O_2). Single carbon nanotubes were manipulated under an optical microscope (100−600×, Nikon Optiphot) with the aid of an *xyz* translational stage (model 462: Newport, Irvine, CA), similar to the methods described in refs 22 and 23.
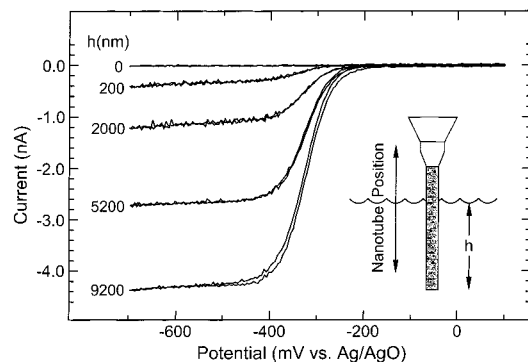
Figure 2. CVs from an uninsulated 150-nm diameter nanotubular electrode in 5 mM Ru(NH$_3$)$_6$ + 0.1 M K$_2$SO$_4$ (v = 100 mV/s). CVs indicate near-ideal radial diffusion with limiting currents that scale with immersion depth, h.
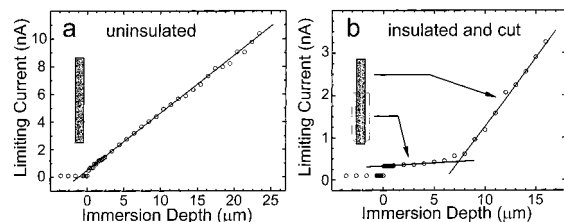

Figure 3. Limiting current as a function of immersion depth for the electrode used to obtain the data shown in Figure 2: (a) uninsulated and (b) insulated-and-cut nanotubular electrodes. Current is recorded as the electrode is raised, and the zero-depth is chosen as the point where the electrode just pulls out of solution as indicated by zero limiting current thereafter. Other conditions were the same as in Figure 2.

tubular electrode at several immersion depths.[26] The sigmoidal voltammograms, which show scan-rate-independent limiting current (up to 1 V/s), are characteristic of radial diffusion to spherical ultramicroelectrodes.[27] This behavior is consistent with fast electron transfer between Ru(NH$_3$)$_6^{3+}$ and the amorphous carbon surface[28] and a diffusion-layer thickness greater than the electrode length or the immersion depth.[29]

The limiting current, i_{lim}, at the uninsulated nanotubular electrode varies linearly with immersion depth, h (part a of Figure 3). The intercept of the best-fit line is 0.39 nA, which represents current from the end of the electrode. In comparison, the theoretical limiting current for a disk electrode of the same diameter is only 0.10 nA.[30,31] The discrepancy arises from a nonideal cut and a finite immersion depth before pull-out, which results in greater than expected area for the nanotube end.

The slope of the best-fit line for this pull-out experiment is 0.41 nA/μm, very close to the value (0.37 nA/μm) expected for an infinitely long cylindrical microelectrode.[31,32] However, this diffusion model is not strictly correct at small immersion depths (vide supra) where the diffusion-layer thickness is on the order of the electrode length.[29] Indeed, we did not observe the characteristic signatures of radial diffusion to cylindrical ultra-microelectrodes (i.e., slightly peak-shaped CVs having a distinct hysteresis between the forward and backward scans)[33] until the immersion depth was greater than ~15 μm. To our knowledge, the particular length/diameter combination of our nanoelectrodes represents an ultra-microelectrode geometry that has not been analyzed theoretically.

Part b of Figure 3 shows a plot of i_{lim} vs h after insulating the lower 8 μm of the electrode with polyphenol. The near-zero slope (0.02 nA/μm) for h < 8 μm (the insulated region of the electrode) demonstrates the effectiveness of the insulation. Previous attempts at coating carbon-fiber microelectrodes (as distinct from nano-tubes) with phenol-containing polymers have produced mixed results, especially in terms of applicability to single-cell analysis.[4,34] Our method differs from previously reported procedures in that the polymerization was initiated in a strongly acidic medium that does not contain a cross-linking allyl phenol. This results in thinner, less permeable coatings than can be achieved by polymerization at high pH.[35] The constant current (0.22 nA) in the flat-current region of this plot (part b of Figure 3) arises entirely from the exposed tip. The deviation of this current from the predicted value (0.10 nA)[30,31] for a 150-nm diameter disk electrode indicates again that the cut at the electrode end is not perfect. Despite this small nonideality, our results are fully consistent with the electrode configurations depicted in Figure 1.

In summary, we have demonstrated that electrochemical nanotubular electrodes can be constructed from single carbon nanotubes. Insulated electrodes of arbitrary length with 80−200-nm diameters can be routinely fabricated. These electrodes represent a new application of carbon nanotubes that takes advantage of their geometrical shape, mechanical strength, and electrical conductivity. We will report shortly on applications of these new electrodes to scanning electrochemical microscopy and bioelectrochemistry.

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(29) The diffusion layer thickness is 14 μm as calculated according to $\sqrt{Dt}$, where D is the diffusion coefficient (7.1 × 10^{-6} cm^2/s, see: Chaila-pakul, O.; Crooks, R. M. *Langmuir* **1995**, *11*, 1329−1340) and t, or RT/Fv, is the time scale of a CV experiment (see Bard, A. J.; Faulkner, L. R. *Electrochemical Methods: Fundamentals and Applications*; Wiley: New York, 1980; p 435). Other relevant symbols are defined as: R the ideal gas constant, T the temperature (298 K), F the Faraday constant, and v the scan rate (100 mV/s).

(30) The limiting current for a disc microelectrode is $2dnFDC$, where d is the electrode diameter (150 nm), n the number of electrons transferred, and C the bulk concentration of the electroactive species (5 mM).

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(32) The slope for a cylindrical electrode can be approximated as $4\pi nFDC/\ln(16Dt/d^2)$, where d is the diameter of the cylinder.

(33) These features are verified in simulated CVs for an infinitely long cylindrical geometry using Feldberg's DigiSim program (see: Rudolph, M.; Reddy, D. P.; Feldberg, S. W. *Anal. Chem.* **1994**, *66*, 589A−600A).

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