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 electrodes can be selectively insulated with a thin layer of polymer 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) and electrochemical analysis of biological materials.

Interest in carbon nanotubes stems from their unique geometrical, mechanical, electronic, and chemical properties. To date, most fundamental research on nanotubes has been focused on their growth mechanism, their sorption properties, refinement of production and purification methods, and direct measurements of various physical properties. Practical applications have also been considered but have so far been limited to their use as tips in scanning probe microscopy (SPM).

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 nanotube electrode and transmission electron microscopy (TEM) images of several electrodes that reveal details about the electrode microstructure. 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). 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 polypyrrole 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 K2SO4 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(NH3)63+ obtained at an uninsulated 150-nm diameter nano-
Spherical ultramicroelectrodes. This behavior is consistent with current (up to 1 V/s), are characteristic of radial diffusion to voltammograms, which show scan-rate-independent limiting carbon surface and a diffusion-layer thickness greater than the fast electron transfer between Ru(NH$_3$)$_6^{3+}$.

The discrepancy arises from a theoretical limiting current for a disc microelectrode is 2 $i_{lim}$ = $i_{lim}$, 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 constant 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.

An uninsulated 150-nm diameter nanotubular electrode in 5 mM Ru(NH$_3$)$_6^{3+}$ + 0.1 M K$_2$SO$_4$ ($u = 100$ mV/s). CVs indicate near-ideal radial diffusion with limiting currents that scale with immersion depth, $h$.

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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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 ultramicroelectrodes (i.e., slightly peak-shaped CVs having a distinct hysteresis between the forward and backward scans) 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) demonstrates the effectiveness of the insulation. Previous attempts at coating carbon-fiber microelectrodes (as distinct from nanotubes) 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 that 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.

The limiting current, $i_{lim}$, can be approximated as 4 $i_{lim}$ = $i_{lim}$, $C$ the bulk concentration of the electroactive species (5 mM), and $t$, or RT/4 $i_{lim}$, 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).

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. Electrochim. Acta 1992, 323, 53–76.


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