Aligned Coaxial Nanowires of Carbon Nanotubes Sheathed with Conducting Polymers**

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The discovery of carbon nanotubes by Iijima in 1991[1] has generated enormous interest in carbon materials and nanotechnology. Since then, carbon nanotubes have been demonstrated to possess exceptional electrical, mechanical, and thermal properties, which are attractive for diverse potential applications ranging from nanoelectronics to biomedical devices.[2–4] On the other hand, it is known that one-dimensional quantum nanowires play important roles, both as interconnecting and active components, in optoelectronic nanodevices and that their orientation has a significant impact on the performance of these devices.[5] The scope for using carbon nanotubes in practical applications, however, has been largely limited by their poor processability (namely, they are insoluble and infusible).[2, 6] Apart from possible improvements in the mechanical and electrical properties of polymers, the formation of nanotube/polymer composites has been and is still being explored as a promising approach for an effective incorporation of carbon nanotubes into devices.[7–11] All studies on the carbon nanotube/polymer composites reported so far are based on randomly entangled nanotubes. The use of perpendicularly aligned carbon nanotubes[2] should offer additional advantages to many applications, which includes electron-emitting flat-panel displays and electromechanical actuators.[12]

We have recently developed simple but effective methods both for producing aligned carbon nanotubes normal to a quartz glass plate, by pyrolyzing iron(II) phthalocyanine ($FeC_{32}N_8H_{16}$, designated FePc) under Ar/H_2 at 800–1100 °C, and for (patterned) transfer of the aligned nanotubes onto other substrates.[13] Herein, we describe that the aligned conducting nanotubes can be used to make novel conducting polymer–carbon nanotube (CP–NT) coaxial nanowires by electrochemically depositing a concentric layer of an appropriate conducting polymer uniformly onto each of the constituent aligned nanotubes. The coaxial structure allows the nanotube framework to provide mechanical stability[3] and efficient thermal and electrical conduction[4, 10] to and from the conducting polymer layer. The large surface and interface area obtained for the nanotube-supported conducting polymer layer is an additional advantage for using them in many optoelectronic applications, for example in organic light-emitting diodes and photovoltaic cells, where the charge injection and separation are strongly limited by the interfacial area available in more conventional devices.[14]

As seen in the scanning electron microscopic (SEM) images shown in Figure 1, we can not only produce homogeneous films of aligned carbon nanotubes by pyrolysis of FePc but also transfer the as-synthesized aligned-nanotube film to a gold substrate with full integrity (Figure 1a) so that electrochemistry can be carried out (see the Experimental Section). The SEM image for the CP–NT coaxial nanowires given in Figure 1b shows the same features as the aligned nanotube array of Figure 1a but with a larger diameter due to the presence of the newly electropolymerized polypyrrole coating in this particular case.

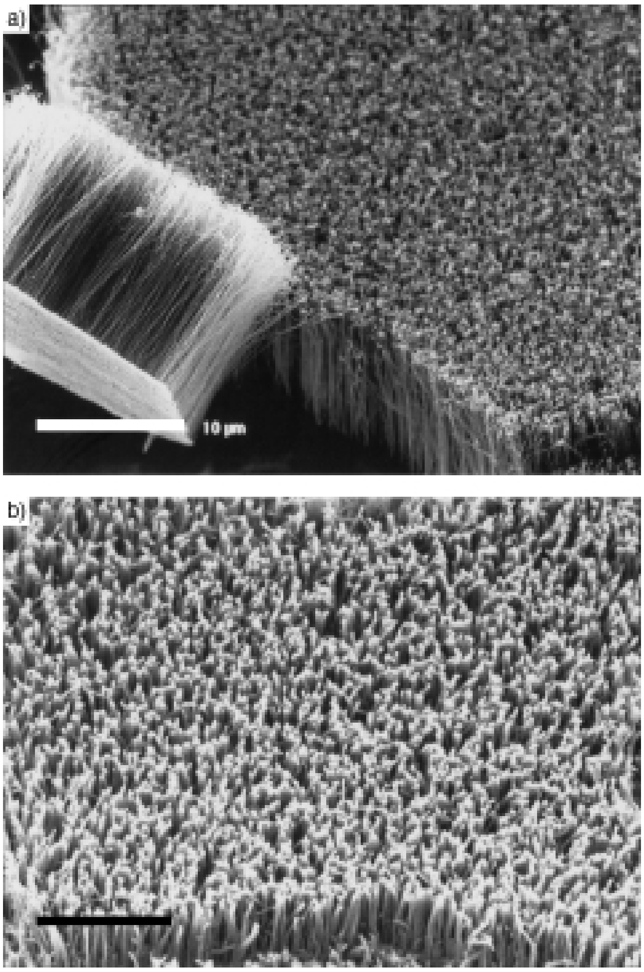

Figure 1. Typical SEM images of: a) aligned nanotubes after transfer onto a gold foil (a small piece of the as-synthesized aligned-nanotube film is included at the bottom-left corner to show the amorphous carbon layer as well; see the Experimental Section); and b) the CP–NT coaxial nanowires produced by cyclic voltammetry (scan rate 25 mV s^{-1}) on the aligned carbon nanotube electrode in an aqueous solution of $NaClO_4$ (0.1 M) containing pyrrole (0.1 M). Scale bar is 10 µm.

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In a typical experiment on the electropolymerization of polyaniline by the cyclic voltammetric method, a current peak at approximately 1.0 V, attributable to aniline oxidation, was observed at the first cycle (Figure 2a). This was followed by the appearance of two new peaks around 0.33 and 0.52 V at a cost of the peak at 1.0 V (Figure 2b). These new peaks can be assigned to the oxidation of polyaniline[15] and the increase in their peak intensity over further cycles indicates a continuous deposition of polyaniline on the nanotube array. Evidence for the formation of the polyaniline layer was also given by the appearance of a greenish color characteristic of polyaniline emeraldine salt in solution around the nanotube electrode. By limiting the number of voltage sweeps, a thin polyaniline layer coating can be deposited along the length of individual nanotubes. Figure 3 show representative transmission electron microscopic (TEM) images taken at the tip (left) and on the wall (right) of a CP–NT coaxial nanowire, which shows an homogenous polymer coating. The thickness of the polymer layer was determined from these TEM images to be about 40–50 nm.

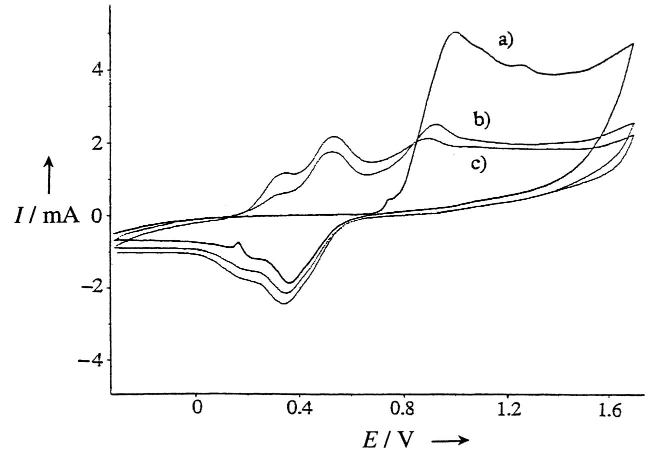

Figure 2. Electropolymerization of aniline (0.1 M) in H_2SO_4 (0.2 M) onto the aligned nanotube electrode. a) First cycle; b) second cycle; c) third cycle. Scan rate is 25 mV s^{-1}.

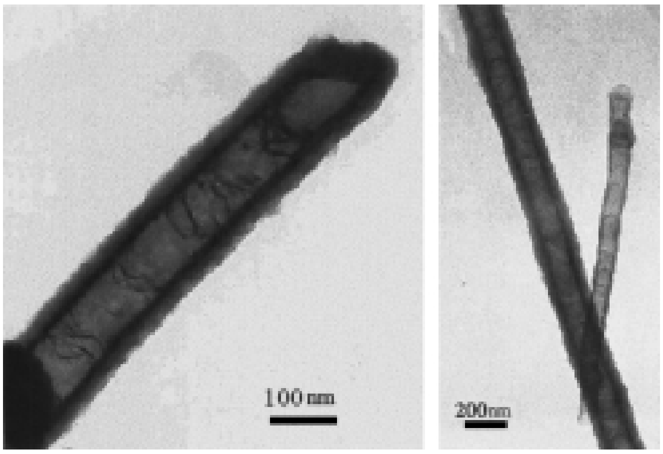

Figure 3. Typical TEM images of the CP–NT coaxial nanowires formed from the cyclic voltammetric method, the images are in the tip region (left) and on the wall (right).

Apart from an even growth of the polymer film, characteristic of electropolymerization of conducting polymers on conventional electrodes (such as on gold or platinium foil),[15] Figure 4a shows a slower growth process around the air–electrolyte interface on a nanotube electrode that was partially immersed into the electrolyte solution. While Figure 4b reveals electrodeposition of a thin conducting polymer layer onto the tips of those nanotubes located near the interfacial region, Figure 4c shows a full encapsulation of individual nanotubes immersed in the electrolyte solution. The observed partial polymer coverage is probably due to a relatively inefficient charge transfer in the interfacial region, coupled with an enhanced local field at the nanotube tips[9] to facilitate the electrodeposition of the conducting polymer layer on top of the nanotube array. The newly formed conducting polymer film then results in a large depletion of the charge at the tip of the nanotubes, which leads to a

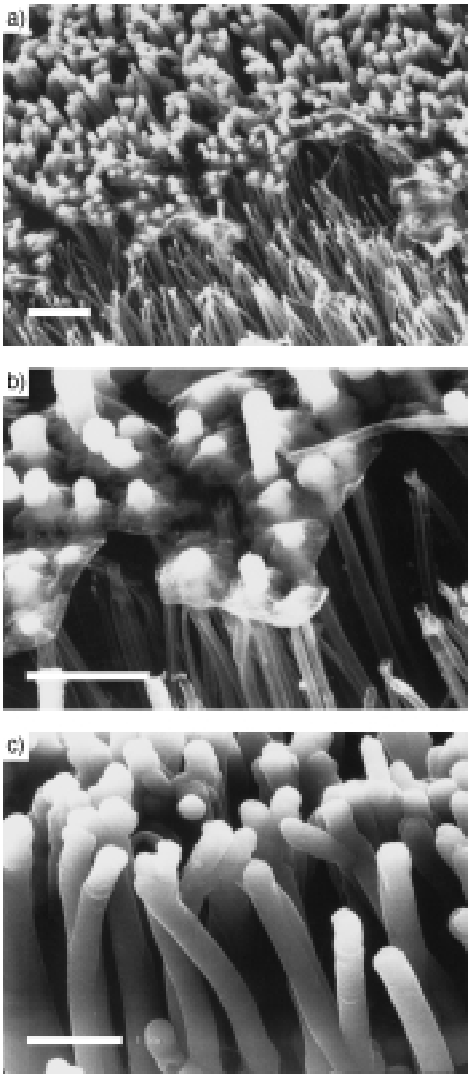

Figure 4. SEM micrographs taken from a nanotube electrode, which was partially inserted into an aqueous solution of $NaClO_4$ (0.1 M) containing pyrrole (0.1 M) after three cycles between −0.6 and 0.6 V (scan rate 25 mV s^{-1}). The images were taken at a) the air/electrolyte solution interface, b) the same position as a) at a higher magnification, and c) immersed in the electrolyte solution. Scale bars are 2 (a) and 1 μm (b, c).

diffusive growth front towards the nanotube base. Under certain conditions, which depend on the nanotube density and monomer and electrolyte concentrations, the non-uniform growth could, therefore, allow the formation of CP–NT coaxial nanowires with only a predetermined portion of the nanotube length being covered by the conducting polymer layer.

To elucidate the chemical structure of the polymer layer, we carried out diffuse-reflectance Fourier-transform infrared and X-ray photoelectron spectroscopic measurements (FTIR, XPS).[16] The electrochemical performance of the aligned CP–NT coaxial nanowires was evaluated by carrying out cyclic voltammetry measurements. As for polyaniline films electrochemically deposited on conventional electrodes, the cyclic voltammetric response of the polyaniline-coated nanotube array in an aqueous solution of H_2SO_4 (1 M; Figure 5 a) shows oxidation peaks at 0.33 and 0.52 V (with similar current densities but much higher peak intensities due to the increased effective surface of the nanotube electrode).[15] As a control, the cyclic voltammetry measurement was also carried out on bare, aligned nanotubes under the same conditions (Figure 5 b). In the control experiment, only capacitive current was observed with no peak attributable to the presence of any redox-active species. Therefore, the polyaniline-coated nanotube composites prepared in this study are highly electroactive. DC conductivity of the polyaniline-coated nanotube film was measured by the standard van der Pauwe four-probe method[19] to be in the order of 10 S cm^{-1}. This value of conductivity is one order of magnitude higher than the polyaniline film electrochemically deposited on a gold plate under the same conditions, possibly due to the "doping" effect associated with carbon nanotubes.[10] Work on the detailed elucidation of charge transport in single CP–NT coaxial nanowires is currently in progress.

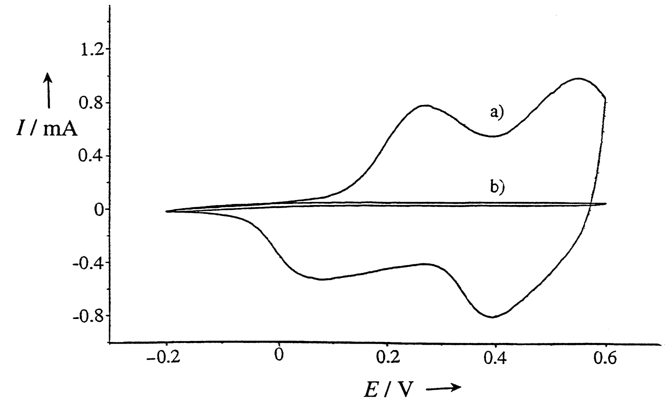

Figure 5. Cyclic voltammograms of a) the polyaniline-coated CP-NT coaxial nanowires and b) the bare aligned carbon nanotubes. Measured in an aqueous solution of 1 M H_2SO_4 with a scan rate of 50 mV s^{-1}.

The newly prepared polymer–nanotube coaxial nanowire is expected to exhibit a high mechanical strength due to the existence of the graphitic framework. This measurement is possible using the electromechanical resonance technique developed recently.[3] For a nanofiber-like structure, a TEM specimen holder was especially built for applying a voltage across the nanotube and its counter electrode. Each single nanotube can be clearly observed in the TEM and the measurements can be done on a specific nanotube whose microstructure is determined by TEM. If a tunable alternating voltage is applied to the nanotube, resonance can be induced. When the frequency of the applied voltage equals the natural frequency of the nanotube, resonance is achieved and the Young's modulus of the nanotube can be obtained from the resonance frequency.[20] For a conducting-polymer sheathed nanotube with an outer diameter of 221 nm, inner diameter of 94.7 nm, and length 9.3 μm, the Young's modulus was determined to be 13.6 GPa, a value which is slightly smaller than that of the nanotube[21] but much higher than the polymer.[22]

The well defined coaxial structure of these highly electroactive aligned CP–NT nanowires, together with the ease with which the conducting polymer coating could be transformed into an *n*- or a *p*-type semiconductor by doping with appropriate electron donors or acceptors,[14] suggests a wide range of potential applications for the CP–NT nanowires, especially in optoelectronic nanodevices and sensors.

Experimental Section

Synthesis: The aligned carbon nanotube films were prepared by pyrolyzing iron(II) phthalocyanine under Ar/H_2 at 800–1100 °C and have been well characterized elsewhere.[13] To construct a gold-supported nanotube electrode for electrochemical generation of the CP–NT coaxial nanowires, we sputter coated a thin film of gold (about 5 μm) onto the amorphous carbon layer covering an as-synthesized aligned nanotube film that was then separated from the quartz glass plate used in the preparation of the nanotube film with an aqueous solution of HF (30 % w/w).[13] In this study, we have used a cyclic voltammetric technique for electropolymerization of aniline (0.1 M aniline/0.2 M sulfuric acid/Milli-Q water) or pyrrole (0.1 M pyrrole/0.1 M $NaClO_4/H_2O$) onto a working electrode of the gold-supported nanotubes (2 × 3 mm^2, MacLab/4E analyser) in a three-compartment cell separated by porous glass. A platinum wire was used as a counter electrode and Ag/AgCl (3 M KCl) as a reference.

Characterization: SEM images were obtained using a Philips XL-30 FEG SEM unit at 5 kV and TEM images were made on a JEOL 100C microscope at 100 kV. FTIR spectra were measured on a Perkin Elmer 2000 spectrometer. Raman scattering measurements were performed on a Renishaw Raman spectrometer using an excitation wavelength of 613 nm. XPS analyses were performed on a Kratos Analytical spectrometer using monochromatic $Al_{K\alpha}$ radiation at a power of 200 W.

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[16] The polyaniline-encapsulated nanotubes gave IR absorption peaks at 1514 (C=C stretching of the benzenoid rings), 1622 (C=C stretching of the quinoid rings), 1359 (C–N stretching), and 1197 cm^{-1} (electronic-like absorption of N=*Q*=N, where *Q* represents the quinoid ring), consistent with reported data.[14] XPS measurements indicated a decrease in the carbon content to 71.08% and concomitant increases to 12.11, 5.81, and 11.00% for nitrogen, sulfur, and oxygen, respectively, after the electrodeposition of polyaniline. The calculated C:N atomic ratio of 6.7 is close to that of aniline (C:N = 6), suggesting the formation of a continuous polyaniline coating with a thickness greater than the XPS detection depth (typically, 10 nm; see Figure 3). The corresponding atomic ratios of 3.8 for O:S and 4.7 for N:S indicated a high doping level of the polymer coating by H_2SO_4.[17] Further evidence for the electrodeposition of polyaniline on the nanotube surface comes from Raman scattering measurements. Whilst the Raman spectrum of the bare nanotubes shows an intense peak at 1584 cm^{-1}, attributable to the E_{2g} mode of the multiwall nanotubes, with a shoulder centered at 1322 cm^{-1} associated with the amorphous graphite,[2] the corresponding Raman spectrum for the polyaniline-coated nanotubes reveals broad bands around 1600, 1495, and 1390 cm^{-1}, typical for polyaniline.[18] An additional peak at 1330 cm^{-1} is associated with the stretching vibration of the -C-N^+-polaron groups, indicating the conducting nature of the polymer coating.

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Living Coordination Polymerization of Allene Derivatives Bearing Hydroxy Groups by π-Allylnickel Catalyst

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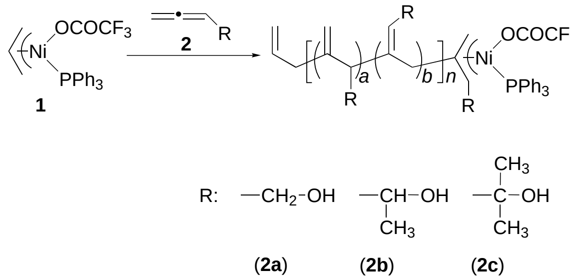
Synthetic polymers such as poly(vinyl alcohol) and poly(2-hydroxyethyl methacrylate)bearing hydroxy groups in their repeating units are, because of their unique polar character and reactivities, useful starting materials for the preparation of many functional compounds. [1] Nevertheless, with the exception of methods that involve the protection and deprotection of hydroxy groups, their use in well-defined synthesis has been limited.[2]

Living polymerization, a technique which is insensitive to polar functional groups on the monomers, is thus a suitable method to prepare well-defined polymers directly from monomers bearing hydroxy groups. The living coordination polymerization of allene derivatives by $[\{(\pi\text{-allyl})NiOCOCF_3\}_2]$ (**1**) is therefore attractive because this complex is able to polymerize monomers having a variety of functional groups, such as alkoxy,[3a–c] aryl,[3d] alkyl,[3e–f] amide,[3g] and carboalkoxy[3h] moieties. Herein we investigate the coordination polymerization of allenes bearing hydroxy groups (**2a**–**2c**) mediated by **1** (Scheme 1).



Scheme 1. Living coordination polymerization of allene derivatives that contain hydroxy moieties (**2a**–**2c**).

The polymerization of 2,3-butadiene-1-ol (**2a**)[4a] by **1** ([**2a**]/[**1**] = 60) was carried out in the presence of PPh_3 ($[PPh_3]/[\mathbf{1}]$ = 1.0) in EtOH at 50 °C (Table 1, entry 1). The polymerization was complete within 3 h and a white powdery polymer (poly(**2a**)) was obtained in 96% yield. The ^{1}H NMR spectrum of poly(**2a**) indicated that it consists of both the 1,2- and the 2,3-polymerized units (labeled *a* and *b* in Scheme 1) in a ratio

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