

## Flexible, Aligned Carbon Nanotube / Conducting Polymer Electrodes for a Lithium-ion Battery

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Carbon nanotubes (CNTs) present a new material for the construction of electrodes. The large scale production of aligned carbon nanotube (ACNT) arrays was first reported by Dai and co-workers [1], providing an opportunity to develop highly ordered, high surface area electrodes with excellent electronic and mechanical properties. While the latter two attributes are realized in the vertical direction, there is a need to develop simple methods of making ACNT composites that are mechanically robust and with sufficient conductivity in the horizontal direction. Such interconnects would give rise to a practically useful electrode structure for use in applications such as energy storage [2], actuators [3] and sensors [4].

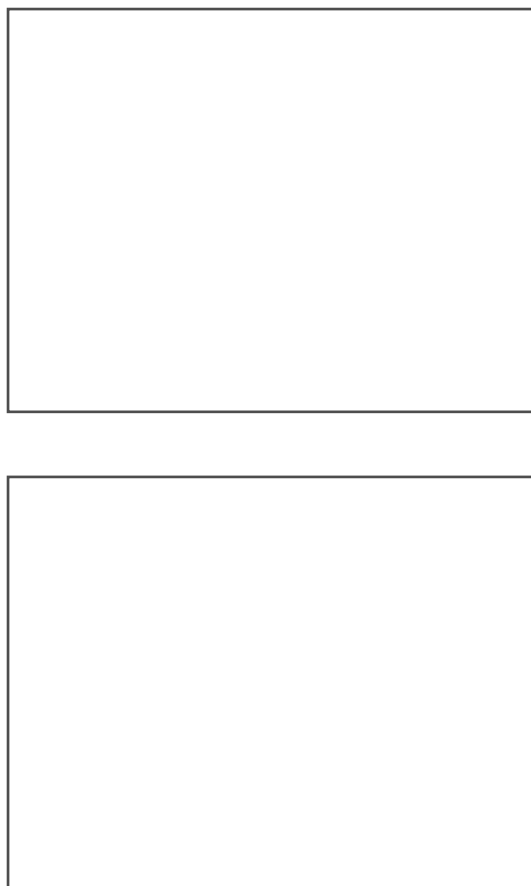
Aligned CNT growth, while producing innovative structures, suffers from a lack of good electrical connectivity between the aligned tubes. Growth on conducting substrates which would provide this electrical connection has met with limited success; recently direct growth on metal alloys [5] has been reported. Depositing metals selectively on top of CNT arrays to achieve this electrical connection [6] is fraught with difficulties. To realize the potential of these arrays in applications such as flexible displays, their removal from the substrate used for growth is necessary. Invariably, removal of the CNT array from surfaces results in damage, including breakdown of any metal coated on top to achieve an electrical connection. To address this issue of lack of robust electrical connection between nanotubes in an array, we present here an approach for preparing a nanostructured ACNT/conducting polymer composite. Organic conducting polymers have proven to be useful in the development of polymer-based composites [7-9]. In the novel nanostructure created here, the CNT's are held together by a conducting polymer composite layer. The nanotubes remain vertically oriented and protrude from the conducting polymer layer (90 % of the tube length is exposed). The electrochemistry of the nanostructured electrodes produced and their use as the anode material in Li-ion batteries are presented.

In this study, poly(3,4-ethylenedioxythiophene) (PEDOT) was utilised as the conducting polymer due to the excellent electrochemical activity and electronic conductivity attainable with this material. A thin PEDOT film was deposited onto the ACNT array by chemical vapour phase polymerization (CVP). The procedure used to form the nanostructured electrode from a quartz plate is summarized in Scheme 1. Aligned multi-wall carbon nanotubes were produced by pyrolysis of iron(II) phthalocyanine as described by Dai [1,10]. Following production of the aligned CNTs on a quartz plate, a thin PEDOT film (100 nm thickness across the entire film) was deposited onto ACNT arrays by CVP using ferric *p*-toluenesulfonate (Fe(III) tosylate) as oxidant. The SEM image of this ACNT/PEDOT composite film (insert (a) in Scheme 1) indicates that the PEDOT deposited by VPP formed a continuous film on the top of the ACNT array. It was found that the PEDOT film was not sufficiently mechanically robust to support the ACNT array. To overcome this problem, a second coating, consisting of poly(vinylidene fluoride) (PVDF), was cast onto the PEDOT film from a 10% (w/w) PVDF acetonitrile solution. The PVDF layer (0.5 μm thickness across the entire film) provided the mechanical robustness required to peel the resultant flexible electrode film from the quartz plate. An example of this free-standing, highly flexible composite is shown in insert (b) of Scheme 1. The composite film could be rolled up without any visual signs of degradation. The resulting free-standing and flexible ACNT-based membrane electrode was then used as the anode material in a rechargeable lithium-ion battery.

[pic]

**Scheme 1.** Illustration of the procedures for the preparation of a free-standing and highly conductive ACNT/PEDOT/PVDF membrane electrode: (a) spin-coating a thin iron (III) tosylate film onto an ACNT modified quartz plate; (b) CVP growth of a PEDOT film on the top of ACNT forest; (c) casting of a thin PVDF film; and (d) electrode structure peeled from the quartz plate as a free-standing robust material.

Scanning electron microscopy (SEM) images (Fig.1) of the ACNT/PEDOT/PVDF membrane electrode show a clear array structure (Fig.1a) supported by a PEDOT/PVDF composite film. The roots of the carbon nanotubes are held tightly by the underlying PEDOT/PVDF layer (Fig.1b, obtained for a stretched (15% strain) electrode). Even upon straining the ACNT/PEDOT/PVDF electrode structure remains intact, highlighting the robustness of the composite electrode. The aligned carbon nanotube layer was found to be adherent and was not removed by rubbing or abrasion on a hard surface.



**Figure 1.** SEM images of ACNT/PEDOT/PVDF membrane electrodes; (a) after peeling (subsequent to stretching), and (b) deliberately stretched (( 15%).

The conductivity of the ACNT/PEDOT/PVDF electrode was determined using a standard 4-probe system (Jandel Model RM2). The ACNT/PEDOT/PVDF membrane electrode had an electronic conductivity over  $200 \text{ S cm}^{-1}$ , which is significantly higher than that measured for an ACNT/PVDF electrode (between  $2$  to  $20 \text{ S cm}^{-1}$ ) prepared under identical conditions without the conductive PEDOT layer in the middle. This result is an average of 10 measurements across the sample, with less than 10% deviation between each measurement, which demonstrates the uniformity of the film structure. The PEDOT layer is obviously critical in producing interconnectivity between the aligned parallel tubes.

The electrochemical characteristics of the ACNT/PEDOT/PVDF nanostructured electrode were determined using a three-electrode cell filled with  $1.0 \text{ M NaNO}_3/\text{H}_2\text{O}$  and comprising a working electrode (ACNT/PEDOT/PVDF), an auxiliary electrode (platinum mesh), and an Ag/AgCl reference electrode. The cyclic voltammogram (CV) (Fig. 2(1)) shows a rectangular shape, indicative of the highly capacitive nature of the ACNT/PEDOT/PVDF electrode with rapid charge/discharge characteristics [11] when compared with PEDOT/PVDF (Fig. 2(2)). This electrode was cycled for 50 cycles and no obvious degradation was observed.

Using methods described elsewhere [12], a  $1 \text{ cm}^2$  nanostructured ACNT/PEDOT/PVDF electrode was assembled into a lithium-ion battery for testing (Neware, Electronic Co.). The Lithium-ion testing cell was assembled in an argon-filled glove box (Mbraun, Unilab, Germany) by stacking a porous polypropylene separator containing liquid electrolyte between the ACNT/PEDOT/PVDF electrode and a lithium foil counter electrode. The electrolyte used was  $1.0 \text{ M LiPF}_6$  in a 50:50 (v/v) mixture of ethylene carbonate and dimethyl carbonate supplied by Merck KgaA, Germany. The cell was cycled between  $0.0$  and  $2.0 \text{ V}$  at a constant current density of  $0.1 \text{ mA cm}^{-2}$ .



**Figure 2.** Cyclic voltammogram of (1) ACNT/PEDOT/PVDF, and (2) PEDOT/PVDF membrane electrodes in 1.0 M NaNO<sub>3</sub>/H<sub>2</sub>O at a scan rate of 20 mV s<sup>-1</sup>.

The typical charge-discharge (Inset (a) in Figure 3) profiles display stable charge-discharge curves during cycling; indicative of stable electrochemical performance by this free-standing ACNT/PEDOT/PVDF membrane electrode. The discharge capacity versus the cycle number for the above cell is shown in Fig.3. The first cycle of this electrode exhibits an enormous irreversible capacity, which can be attributed to the formation of a solid electrolyte interface (SEI) layer on the surface of the electrodes [13]. However, a highly stable discharge capacity of 265 mAh g<sup>-1</sup> is observed after 50 cycles. This is significantly higher than the value obtained previously for SWNT paper (173 mAh g<sup>-1</sup>) under identical working conditions [14]. This is attributed to the high accessible surface area of the aligned carbon nanotubes which, coupled with the robust polymer layer, provides a mechanically stable array. The CNTs in ACNT/PEDOT/PVDF electrode keep their nanostructured architecture, while the CNTs in SWNT paper prepared via vacuum filtration aggregate to form a bundle of CNTs and thereby lessen the surface area of the electrode. This is reflected in the stable long-term electrochemical performance of these electrodes in a Li-ion battery. No degradation was observed over 50 charge-discharge cycles.

Another significant improvement is that this free-standing ACNT/PEDOT/PVDF electrode with excellent electronic and mechanical properties does not require a metal substrate (copper foil) as is normally employed to support the active materials in a Lithium-ion battery [15]. For a typical anode (1 cm<sup>2</sup>) this equates to 14 mg of copper compared to 2 mg of PVDF, which still could be decreased by optimizing the process. This would significantly decrease the weight of the anode in a lithium-ion battery, or allow more active material per unit mass to increase the capacity per battery unit. The other advantage of this copper-free electrode is that it may contribute to the improvement of the long-term battery performance; without copper dissolution caused by impurities in the electrolyte. Due to the chemical and electrochemical stability of PEDOT and PVDF, the impurities in the electrolyte would not cause the same problem as that for copper foil during the long-term battery performance. This may explain the stable electrochemical performance observed when used in a Lithium-ion battery.

[pic]

**Figure 3.** Discharge capacity vs. the cycle number of ACNT/PEDOT/PVDF electrode in a Li-ion testing cell under a constant current density of 0.1 mA cm<sup>-2</sup>.

Our preliminary results indicate that this novel “free-standing” ACNT/PEDOT/PVDF membrane electrode, which is lightweight, flexible, highly conductive, and mechanically robust, could be easily fabricated into a rechargeable battery without using a metal substrate or binder. In this Li-ion battery, the weight of the electrode is reduced significantly compared with a conventional electrode made by coating a mixture containing an active material onto the metal substrate. The results also show that the capacity of the ACNT/PEDOT/PVDF electrode is 50% higher than that observed for free-standing SWNT paper. This study has important implications for the use of aligned carbon nanotube/conductive polymer composites as a new class of electrode materials in developing flexible rechargeable lithium-ion batteries and may lead to other applications of carbon nanotubes in flexible electronic devices. The scale-up production of ACNT for increasing the power of single-cell is under investigation.

#### Supporting Information

In a typical experiment following production of the aligned CNTs on a quartz plate, PEDOT film was deposited onto the CNT array by chemical vapour phase polymerisation. A thin film of ferric *p*-toluenesulfonate (Fe(III) tosylate) was coated on the ACNT array using a spin coater (Laurell Tech. Co.) at a speed of 1000 rpm for 1 min from a 10% (w/w) Fe(III)

tosylate solution in ethanol. The Fe(III) tosylate coated ACNT array was placed directly into an oven at 80°C for 3 min to quickly evaporate the ethanol, thereby forming a good quality continuous Fe(III) tosylate film. The sample was then exposed to 3,4-ethylenedioxythiophene (EDOT) monomer vapour in the vapour phase polymerization (VPP) chamber at 60°C [16]. After 30 min, the sample was removed from the chamber and a blue film was visible on the quartz plate indicating the formation of PEDOT. Following air-drying for 1 h, the PEDOT coated ACNT array was washed in pure ethanol to remove unreacted EDOT monomer as well as Fe ions. The PEDOT modified ACNT array was then dried in a fume-hood.

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## Quartz plate

Iron(III) tosylate film

Insert (b)

(a) Spin-coating

Insert (a)

ACNTs

(b) CVP of PEDOT

PEDOT film

(c) Casting of PVDF

PVDF film

PEDOT film

(d) Peeled off

ACNTs

PVDF film

PEDOT film

(a)

ACNT

PEDOT/PVDF

(a)

(b)

(2)

(1)

PEDOT/PVDF

ACNT