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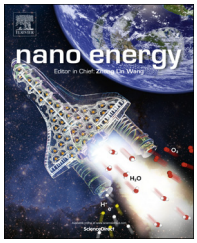

RAPID COMMUNICATION

# Roll-to-roll synthesis of vertically aligned carbon nanotube electrodes for electrical double layer capacitors

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**Abstract**
Research in carbon nanomaterials has seen tremendous growth in recent years; however, technological advances are limited by the lack of continuous and scalable synthesis methods. Here we present a scalable roll-to-roll process for synthesizing vertically-aligned multi-walled carbon nanotubes (VACNTs) on Al foil ribbons which are continuously drawn through a chemical vapor deposition (CVD) reactor operating at ambient pressure and a relatively low growth temperature (600 °C). Electrodes comprised of VACNT forests synthesized in this process are directly assembled into supercapacitor cells, which yield high power densities (1270 W/kg) and energy densities (11.5 Wh/kg). These devices exhibit excellent cycle stability with no loss in performance over more than a thousand cycles.
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## Introduction

Electrochemical double layer capacitors (EDLCs), also known as supercapacitors, have emerged as a promising solution for applications requiring durable and reliable devices with high power and energy density [1,2]. EDLCs offer comparable power densities to electrolytic capacitors while providing 2 to 3 orders of magnitude increase in energy density, thus allowing them to complement or serve as possible replacements for existing batteries [3]. Due to the prevalent use of activated carbon electrode materials, EDLC performance is often correlated with the electrode surface area, in which pore size distribution and the solvated electrolyte ion radius define the accessibility [4]. In this regard, the unique properties of carbon nanotubes (CNTs) make them suitable candidates for EDLC electrodes [5]. While the electrochemical stability of CNTs is necessary for long lifetime EDLCs, their high electrical conductivity allows for better electron transfer to the current collector and their high surface-to-volume ratio provides greater ion access [4]. Accordingly, vertically aligned arrays of multi-walled CNTs (VACNTs) have been considered for use in EDLCs due to their facile synthesis and the ability to control the ion-accessible surface by varying the CNT areal density on growth substrates [6–10]. VACNT electrodes have been used to achieve high power density EDLCs [11]; however, continuous synthesis methods to prepare VACNTs directly on current collectors (e.g., Al foil) at relatively low costs are needed for commercially viable high power and high energy density EDLCs. Additionally, when CNTs are grown from catalyst particles that are adhered to the current collector, the need for a binder is eliminated, thereby reducing inactive weight and contact resistance [4].

Although CNTs can be synthesized in large quantities, present processes are not amenable for VACNT growth directly on current collectors for scalable manufacturing of EDLC electrodes [12]. Since the discovery of CNTs, several methods have been pioneered for their production, including electric arc discharge [13,14], laser ablation [15,16] and chemical vapor deposition (CVD) [17,18], however, only CVD has emerged as a practical and reliable method for synthesizing VACNT forests. While the CVD method is relatively versatile in terms of controlling CNT characteristics (e.g., tube diameter, number of walls, and dopant ratio) [19,20], three factors that limit large scale VACNT synthesis are: (i) substrate size set by reactor geometry, (ii) requirements of a complex catalytic substrate preparation, and (iii) high operating temperatures that are incompatible with traditional current collectors (e.g., Al foil).

Previously, Andrews et al. developed a ferrocene–xylene liquid injection floating catalyst technique to grow VACNT forests on bare $SiO_2$/Si or quartz substrates, greatly simplifying the synthesis process [21]. Considering the startup and shutdown times for batch processing (which often consume >95% of runtime), a continuous roll-to-roll (R2R) process is expected to greatly reduce time, energy, and cost needed to produce VACNT forests [22]. Here, we describe a commercially viable low temperature R2R process for growing VACNTs on inexpensive Al foil current collectors to achieve continuous production of CNT-based EDLC electrodes. Our electrochemical studies on single electrodes show that VACNT forests produced using our R2R method exhibit nearly four-times higher capacitance (~50 F/g) than randomly entangled buckypapers prepared from commercial CNTs (~13 F/g). Additionally, VACNTs produced using our R2R method displayed significantly lower contact resistance compared to CNT buckypapers. More importantly, we observed that symmetric supercapacitors comprised of R2R-produced VACNT electrodes exhibited high power densities (1270 W/kg) and energy densities (11.5 Wh/kg) with no loss in performance over more than a thousand cycles, compared to CNT buckypapers (650 W/kg and 5 Wh/kg).

## Materials and methods

Tetrabutylammonium hexafluorophosphate ($TBAPF_6$, 98%) and tetraethylammonium tetrafluoroborate ($TEABF_4$, >99%) were purchased from Sigma Aldrich. Acetonitrile (Certified ACS) and propylene carbonate (99%) were obtained from Fisher. O-xylene (98%) and ferrocene (98%) were purchased from Sigma Aldrich. Al foil substrates were purchased from Aldrich (99.9%) or from the local grocery store (Reynolds). Multi-walled Carbon Nanotubes (30–50 nm outer diameter) were purchased from CheapTubes.com. Celgard separators (2325, 25 μm microporous trilayer PP/PE/PP membrane) were provided by Celgard.

### Stationary CVD process

VACNT arrays were grown by CVD in a quartz tube with diameter of 2″. Both ends of the tube were closed with stainless steel end-caps. The tube was placed in a furnace with two heating zones (reacting zone-40″, and preheating zone-20″). A programmable syringe pump was used to inject the precursor (ferrocene in xylene, 0.5 at% Fe), with the tip of the injection nozzle located at the center of the preheating zone. Al foils (Reynolds Wrap, 2 cm × 15 cm) cleaned with acetone were placed in the center of the reacting zone of the furnace. The system was heated up to 600 °C under a flow of Ar (500 sccm)/$H_2$ (100 sccm). At 600 °C, the precursor was injected into the tube at a rate of 1.5 ml/h, along with $C_2H_2$ (30 sccm).

### R2R process

VACNT arrays were grown using ambient pressure CVD in a Lindbergh Blue tube furnace that has an active zone of approximately 24 cm. The Al foil (Reynolds Wrap) which is used as the substrate is first swabbed clean with acetone. Al foil ribbon is then threaded through the quartz reaction tube and attached to the uptake spool before allowing the system to heat to 600 °C under 500 sccm of Ar. Once the reaction temperature (600 °C) was reached, the uptake motor was activated to reel the foil at a rate of 0.5 cm/min. $H_2$ and $C_2H_2$ are then introduced at 50 sccm and 30 sccm respectively, as well as the precursor solution of 0.5 wt% ferrocene in xylene, which was injected into the tube at 0.3 ml/h using a programmable syringe pump (New Era NE-1000).

### Preparation of CNT buckypapers (BP)

CNTs (CheapTubes.com) were dispersed in 1% aqueous solution of sodium dodecyl sulfate (SDS) using a tip sonicator

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