BISCROLLED CARBON NANOTUBE COMPOSITE YARNS FOR MULTIFUNCTIONAL APPLICATIONS IN ENERGY CONVERSION AND STORAGE

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Keywords: *Carbon nanotube yarn, multifunctional, battery, fuel cell, electronic textile*

1 Introduction

Though yarn spinning has prehistoric origins and remains vital today, a host of important materials cannot be made into yarns by previously known methods. Generically applicable methods are here described for producing continuous yarns comprising up to 99 wt % of otherwise unspinnable nanopowders or nanofibers that remain highly functional [1]. These methods utilize the strength and electronic connectivity of sometimes minute amounts of carbon nanotube sheets that are helically scrolled in the yarns. Scrolled 50 nm thick nanotube sheet or sheet stacks can confine nanopowders, micropowders, or nanofibers in the corridors of often irregular scroll sacks, whose observed complex structures are related to twist-dependent extension of Archimedean or Fermat spirals or spiral pairs into scrolls. This new technology is used to make yarns of graphene ribbons, superconductors, high performance battery materials, catalytic oxygen electrodes for fuel cells, TiO_2 for release of active oxygen, and strong sutures containing biomedical agents. The observed mechanical properties enable yarn knotting and the weaving and sewing of biscrolled multifunctional yarns into textiles.

2 Fabrication of Biscrolled Yarns

Biscrolling begins with fabrication of a guest/host stack by depositing guest material onto (a) a CNT sheet wedge directly produced by twist-based spinning from a CNT forest [2] or (b) forest-drawn CNT sheets [3]. Guest deposition onto a CNT web using an electrostatic powder coating gun is fast and controllable due to attraction between charged guest particles and the oppositely charged web. Other liquid-free guest deposition processes include electron beam evaporation, sputtering, and aerosol filtration. Liquid-based guest deposition also works, like using a MWNT sheet stack as a filter to capture liquid-dispersed powders; electrophoretic deposition; and ink-jet printing. The process for biscrolled yarn fabrication ends with twisting a bilayer guest/sheet stack to make yarn. Figure 1 shows a schematic diagram of the fabrication of biscrolled yarns by using host/guest (HG) stacks that can be by liquid-free guest deposition or liquid-based approach, and both including a last step to insert twist in the HG stack (in the case of liquid approach necessary to remove the filtration membrane).

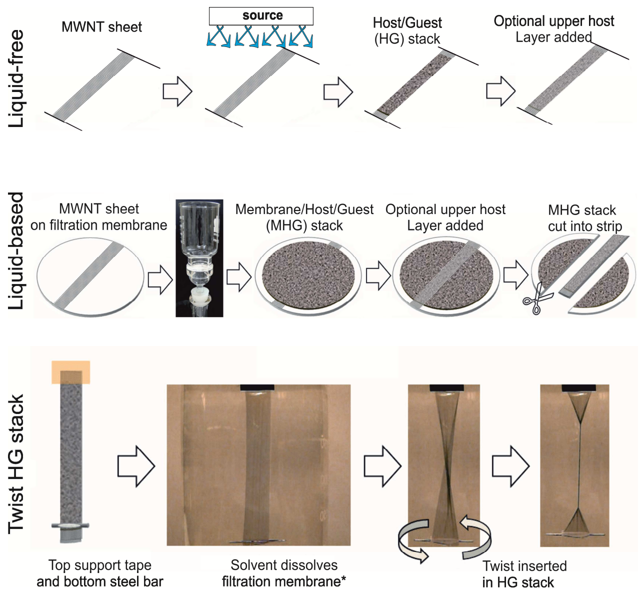

Fig. 1. Illustrations of: liquid-free guest material deposition, wet vacuum-filtration guest deposition and liquid-bath-based twist insertion processes for biscrolled yarn production.

3.0 Structure Development and Transitions for Scrolled and Biscrolled Yarns

We have discovered that fundamentally different nanotube yarn structures are produced by changing spinning conditions and resulting parameters (like end constraints, stress asymmetry during spinning, spinning wedge base width, and “wedge angle”, the total apex angle where the wedge converges to yarn). The observed structures are related to Archimedean and Fermat spirals and more complicated inter-connected spirals. Accordingly, ignoring the radial dependence of interlayer spacings, we name structures observed for biscrolled and guest-free yarns as Archimedean, Fermat, and dual Archimedean scrolls. “Archimedean” means that a sheet edge is buried deep in a scroll and “dual Archimedean” means that sheet edges are buried in different interconnected scrolls. An ideal Fermat scroll has both sheet edges on the yarn surface. Scanning electron microscope (SEM) images of spinning wedges in Figure 2, show Fermat scrolling (A) and Archimedean scrolling (B) during twist insertion while drawing directly from the CNT forest.

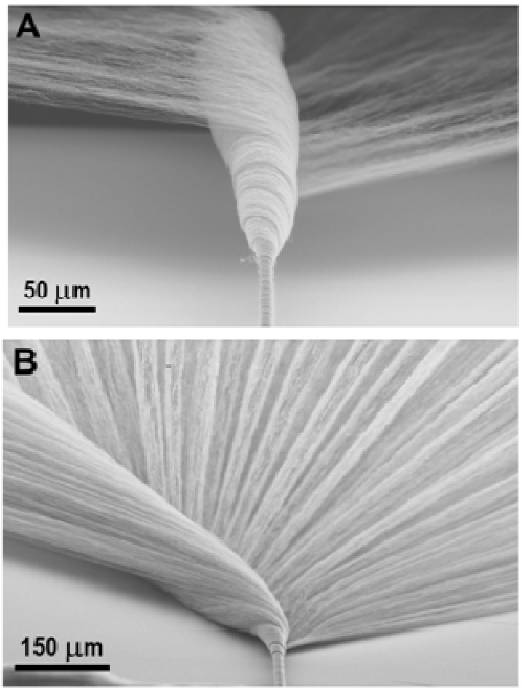

Fig. 2. SEM micrographs showing an oblique view of a guest-free yarn that is undergoing Fermat scrolling (**A**) and Archimedean scrolling (**B**) [1].

4.0 Processability of Biscrolled Yarns

Even when a very small amount of CNT host mechanically confines an otherwise unbonded powder guest, biscrolled yarns can be knotted and sewn as shown in Figure 3.

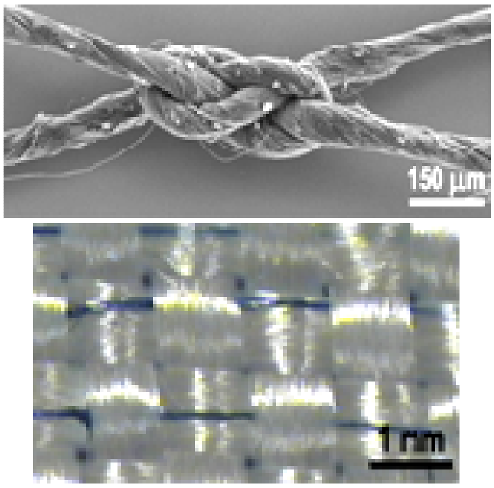

Fig. 3. Top: SEM image of a carrick bend knot between two biscrolled yarns made of 88% silicon oxide (SiO_2) deposited onto 3 MWCNT sheets (SiO_2@$MWNT_{3,0}$). Bottom: Photograph of a biscrolled yarn consisting of 85% TiO_2 powder deposited onto 3 MWCNT sheets (TiO_2@$MWNT_{3,0}$) that has been hand sewn into Kevlar® textile [1].

Experiments also show that a biscrolled yarns containing 93 wt % TiO_2 can be attached to a textile and washed in an ordinary washing machine without measurable (> 2 wt %) loss of guest or strength change.

5.0 Energy Related Applications of Biscrolled Yarns

Superconducting yarn was obtained by biscrolling a mixture of magnesium and boron powders as guest on MWNT sheets (Figure 4). One percent CNT host held 99 wt % of these precursors during twist insertion and harsh chemical treatment, despite the large B and Mg particle diameters (~40 µm) compared with the ~50 nm thickness for densified MWNT sheet. Four-probe electrical conductivity measurements show that the biscrolled yarn becomes superconducting at the expected critical temperature (39 K) for MgB_2 [4]. This method for making superconducting yarn avoids the over 30 drawing steps needed to produce millimeter diameter, iron-clad superconducting wires from Mg/B/MWNT precursor using the powder-in-tube method [5].

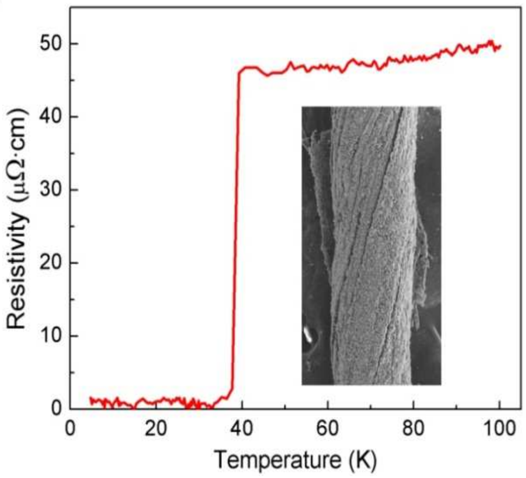

Fig. 4. Electrical resistivity *versus* temperature for superconducting biscrolled yarn, showing T_c=39 K. (Inset: SEM image of the 170 μm diameter yarn. This yarn contains 98 wt % MgB_2 that is in the helical corridors of 2 wt % MWNT host) [1].

The performance of biscrolled yarns as flexible battery cathodes was evaluated by using $LiFePO_4$ as guest, which is an inexpensive, environmentally friendly, high performance Li-ion battery cathode material [6]. Charge collection from this high rate, high capacity redox material is an important problem because of its low electronic conductivity, and the nanoscale proximity between highly conducting MWNT host and the $LiFePO_4$ in biscrolled yarns should provide a solution to this problem that minimizes total electrode weight. Figure 5A is a cyclic voltammogram conducted using a Gamry Instruments potentiostat-galvanostat between 2.5 and 4.2 V at a scan rate of 0.1 mV/s, The electrode results are for a 100 μm diameter biscrolled yarn containing 95 wt % $LiFePO_4$ guest, which is weavable and knottable despite this massive powder concentration. Using Li metal as the anode and the total cathode weight to provide normalization for energy and power densities, energy storage densities of 379 Wh/kg and 135 Wh/kg resulted for power densities of 180 W/kg and 4590 W/kg, respectively. Figure 5B is a SEM micrograph for 94% $LiFePO_4$@$MWNT_{2,1}$ showing $LiFePO_4$ particles contacted by a network of MWNTs.

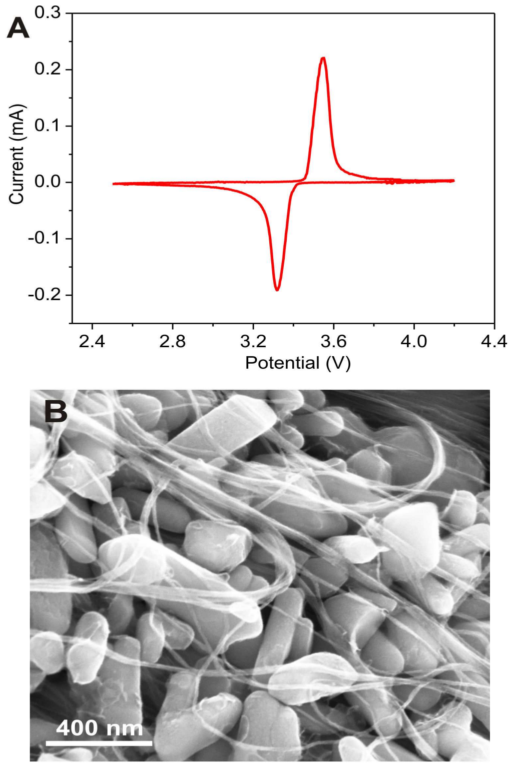

Fig. 5. (**A**) Cyclic voltammogram of a 95% $LiFePO_4$@$MWNT_{4,6}$ biscrolled yarn between 2.5 and 4.2 V (*vs* Li/Li^+) at 0.1 mV/s in an electrolyte containing 1 M $LiPF_6$ in a 1:2:3 by volume mixture of propylene carbonate, ethylene carbonate, and dimethylcarbonate, respectively. (**B**) SEM micrograph of the surface of a 94% $LiFePO_4$@$MWNT_{2,1}$ biscrolled yarn, showing $LiFePO_4$ particles contacted by a network of MWNTs [1].

Since catalytic oxygen reduction is crucial for fuel cells and metal-air batteries, and the cost of noble metal catalysts is a major problem, we next investigated whether nitrogen-doped MWNT (N_xMWNT) guest in biscrolled yarns can provide this catalysis. While N_xMWNT is known to be a promising oxygen reduction catalyst [7] the question is "Can this catalytic activity be retained in a biscrolled yarn that is weavable into a strong, flexible cathode?" Evidence for catalytic activity was obtained by comparing the cyclic voltammetry of biscrolled 91% MWNT guest powder in MWNT host sheets and biscrolled 90% N_xMWNT guest powder in MWNT host sheets. The N-doped

MWNTs (N/C ~0.03) were prepared using a floating catalyst method and purified to remove iron catalyst [8]. The onset potential for oxygen reduction by biscrolled N_xMWNT guest powder shifts by *ca.* +0.3 V with respect to that for biscrolled MWNT guest powder. The same shift in onset potential was observed for the bilayer sheet stack that was precursor to the biscrolled yarn, indicating that biscrolling is not interfering with catalytic activity.

6.0 Upscaling sheet fabrication for biscrolling

At present, we generally draw the nanotube sheets used for biscrolling from nanotube forests that are grown on Si wafers. In order to provide a less expensive process that is suitable for upscaling, we recently demonstrated [9] nanotube sheet fabrication from forests grown on flexible stainless steel (SS) foils (50.8 μm thick SS 321) that could be used as belts for the continuous fabrication of biscrolled yarns. Figure 6A shows a 12 cm by 16 cm area SS foil substrate that has been cylindrically bent, so that it fits within a 65 mm inner diameter quartz furnace tube (with catalyst and buffer layer on the interior side). This use of a flexible SS substrate increased the forest area that can be grown in a given diameter furnace. Even after CNT forest growth the SS substrate is still quite flexible. This enables bending the as-produced forest around small diameter (2.5 cm) mandrels while a CNT sheet is drawn from the forest (Figure 6C).

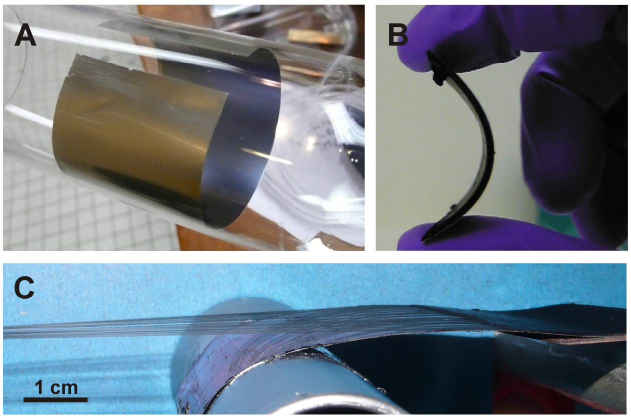

Fig 6. The flexibility of the SS substrate before and after CNT forest growth by thermal CVD: (a) A SS foil bent on the inner surface of the quartz tube used as a reactor chamber for thermal CVD. (b) Millimeter tall CNT forest grown on a flexible SS foil. (c) Photograph of a 5 cm wide CNT sheet being pulled from a forest grown on a bent SS substrate [9].

We also discovered [9] that forest spinnability is insensitive to the surface roughness of our SS foil and that the substrate area utilized for forest growth can be doubled without sacrifice of forest drawability by depositing the buffer and catalytic layers on both faces of the metal foil. These recent results demonstrate that the expensive use of silicon substrates can be replaced by the use of stainless steel substrates for the production of drawable forests, and that the use of these flexible substrates enables substantial increase in the forest area that can be synthesized in a given diameter furnace.

Using the flexible stainless steel sheets as a moving belt, where forest is continuously grown on one part of the belt and stripped off to make nanotube sheets on another part of the belt, commercial scale production of nanotube sheets and yarns and biscrolled nanotube yarns seems feasible. Figure 7 is a schematic diagram of a possible upscaled process.

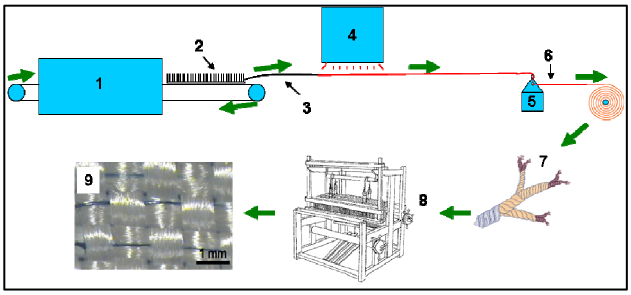

Fig. 7. Schematic diagram of possible upscaled production of multifunctional biscrolled textiles, which shows: (1) CVD growth of spinnable CNTs forests on a moving belt; (2) spinnable CNT forest; (3) CNT sheet; (4) spray-coating or ink jet deposition of guest material over CNTs sheet; (5) spinner; (6) multifunctional biscrolled CNT yarn; (7) biscrolled yarns twisted into single fibers (red), that are spinned into plies (yellow) and twisted into cords (white); (8) loom of cords into textiles; (9) multifunctional textile.

Acknowledgement

Supported by Air Force Grant AOARD-10-4067, Air Force Office of Scientific Research grants FA9550-09-1-0537 and FA9550-09-1-0384, NSF grant DMI-0609115, and Robert A. Welch Foundation grant AT-0029.

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