Multifunctional Yarns and Fabrics for Energy Applications

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Submission date: 5/15/2013

Abstract:

The project focus on developing bicrrolled carbon nanotube yarns and textiles for supercapacitor/battery and fuel cell electrode applications was chosen because of the urgent need for improved technologies for electrical energy storage and fuel-cell-based electrical energy generation. Project provided advances are in electrode electrochemical performance, mechanical robustness, and mechanical flexibility that can enable (1) giant power and energy densities; (2) multifunctional applicability where electrode strength and flexibility is utilized, like for energy storage in structural vehicle panels and electronic textiles; (2) deployability for both ultra-large and very small devices; (3) elimination of noble metal catalysts from fuel cell electrodes; and (4) the ability to harvest and store electrical energy in the human body. Woven textiles that are high performance biofuel cells and redox supercapacitors resulted from program work. While project focus was on fuel cell and energy storage electrodes based on bicrrolled yarns, collaborative US-Korea project research has also provided advances in fabrication, process upscale, and in experimental and theoretical understanding of structure and properties that are important for all applications of bicrrolled yarns. Major project advances in the energy area have also been made on artificial muscles and associated textiles that can be electrically, chemically, or photonically driven, as well as super-tough yarns that can absorb about 6 times higher energy before rupture than spider silk. Some of these artificial muscles can harvest energy from the environment to provide powerful large-stroke actuation. These project advances could not have been made without the realized highly effective partnership of the laboratories of the US and Korea PI’s.
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15. SUBJECT TERMS
nano materials, nano science and technology, nano technology, Nanobiotechnology

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Standard Form 298 (Rev. 8-98)
Prescribed by ANSI Std Z39-18
Introduction:

This final report briefly summarizes progress that we have made in the full NBIT II program and provides a list of NBIT II supported publications and patent filings.

The goals are to (1) provide scientific and technological advances enabling structure/properties optimization and efficient fabrication of the team’s biscrolled multifunctional yarns, thereby providing the basis for their commercialization, especially as fuel cell and battery/supercapacitor electrodes and to (2) demonstrate such superior electrochemical performance for textile-based electrodes woven from biscrolled yarns that next generation supercapacitors/batteries, fuel cells, and biofuel cells are enabled. When opportunities arise, we have exploited our biscrolling technology for other applications of interest for the sponsors in the energy area.

Our approach involves twist-based spinning of carbon nanotube sheets or sheet wedges (the host) that are overlaid with up to 98 wt% of one or more other functional materials (the guest). Whether the overlaid functional guest comprises nanoparticles, nanofibers or larger guests, we have shown that the guest is trapped within the corridors of host scrolls, whose topology is related to Fermat, Archimedean, or dual Archimedean spirals.

Despite the up to 98 wt% of functional powders in the biscrolled yarns, these yarns are weavable, braidable, sewable, knottable, and washable. Most important, the guest powders and nanofibers remain highly functional, which has enabled our fabrication of biscrolled yarn cathodes for Li-ion batteries, catalytic oxygen cathodes for fuel cells, and superconducting biscrolled yarns.

Project Results:

We reported in a 2011 NBIT funded Science publication a new technology\(^1\), called biscrolling, which enables the spinning of “unspinnable” powders and nanofibers into weavable, sewable, knottable, and washable multifunctional yarns that can contain over 92 wt% of functional guest powders. Working with NBIT collaborator Seon Jeon Kim’s team, we most recently developed the basis for continuous solution-based biscrolling (floating sheet biscrolling) and expanded applications of biscrolled yarns from battery and fuel cell electrodes and superconducting yarns to redox supercapacitors, elastomeric electronic and thermal interconnects, strain sensors, biofuel cells, weavable catalyst containers, artificial muscles, and thermal energy storage yarns for textiles. Our NBIT team also made biscrolled yarns by twist insertion in graphene sheets and the first braided biscrolled yarns.

The NBIT collaborators reported in ACS Nano (2011)\(^2\) nanomembrane-based redox supercapacitors that provide exceptional power density (7900 kW/liter), high energy density (70 Wh/liter), and long cycle life. These nanomembranes comprise carbon nanotube sheets in which bundles of individual nanotubes are coated with poly(3,4-ethylenedioxythiophene). Using a modification of our biscrolling technology, we twist spun these nanomembranes into yarn electrodes for supercapacitors. In their most recent work, which is accepted for publication in Nature Communications (2013)\(^3\), our Korea/US team demonstrated 7000 kW/liter power density and 50 Wh/liter energy density for two ply yarns in which one ply is a 20 µm diameter biscrolled yarn and the other ply is about the same diameter metal wire. A novel technology, gradient biscrolling, provides fast-ion-transport yarn in which hundreds of layers of conducting-polymer-infiltrated carbon nanotube sheet are scrolled into 20 µm diameter yarn. Plying the biscrolled yarn with a metal wire current collector increases power generation capabilities. The volumetric capacitance is high (up to 179 F cm\(^{-3}\)) and the discharge current of the plied yarn supercapacitor
linearly increases with voltage scan rate up to 80 V/s and 20 V/s for liquid and solid electrolytes, respectively. The exceptionally high energy and power densities for the complete supercapacitor, and high cycle life that little depends on winding or sewing (92%, 99% after 10,000 cycles, respectively) are important for the applications in electronic textiles. Since the yarns are strong (370 MPa strength), weavable, braidable, knittable and sewable, such outstanding performance is promising for future applications, like electronic textiles and energy-storing panels for vehicles.

Minimizing fuel and oxidant diffusion distances and the separation between current collectors and redox mediators and enzymes is critically important for devising high power biofuel cells. To achieve long life, functional electrode components must be effectively trapped in a highly conducting porous structure. Towards achieving these goals we fabricated biscrolled carbon nanotube yarns electrodes for vascular biofuel cell textiles in which twist-based yarn spinning immobilizes redox mediators and enzymes within scrolled yarn corridors, nanotube conductivity and strength enables current collection and yarn weavability, and small yarn diameters provide fast access of fuel and oxidant. Separator-free biofuel cells made from these biscrolled yarns provide an open circuit voltage of 0.80 V and maximum power densities based on yarn area and volume of 2.31 mW/cm² and 840 mW/cm³, respectively, for glucose energy harvesting, compared with the 1.66 mW/cm³ for recently described high power, disk-type biofuel cells. Scalability to highly vascular biofuel cells that might eventually be implanted in the human body was demonstrated by fabrication of biofuel cell textiles that contain separately woven anode and cathode yarns that contain glucose oxidase and bilirubin oxidase, respectively. This NBIT sponsored work was recently submitted by the Korea/US NBIT team for publication in Nature Communications.

A NBIT supported paper on scrolled yarns comprising highly oriented graphene nanoribbons was recently published in Advanced Materials. The strategy that we successfully deployed to make these graphene nanoribbon yarns is to (1) chemically unzip highly oriented MWNT sheets to make graphene oxide nanoribbons, (2) use surface tension effects to convert the resulting graphene oxide nanoribbon sheets to make graphite oxide nanoribbon yarns, and (3) to reduce these nanoribbon yarns to make graphene nanoribbon yarns. Graphite nanoribbon yarn (obtained by reduction of the graphene oxide yarn with hydrazine and subsequent annealing at 300ºC) provided an outstanding gravimetric capacitance of 99 F/g, which is 5 times higher than that of carbon nanotube yarns obtained by dry spinning from the same forest used to produce the graphene ribbon yarns.

The Korea/US NBIT team have discovered that a mixture of single walled nanotubes (SWNTs) and reduced graphene oxide flakes (RGOF) can be solution spun from aqueous dispersion to directly provide super tough fibers containing poly(vinyl alcohol). The gravimetric toughness approaches 1,000 J/g, far exceeding spider dragline silk (165 J/g) and Kevlar (78 J/g). As described in a NBIT supported publication in Nature Communications, the SWNTs and RGOFs interact during spinning to form an interconnected network of partially aligned SWNTs and RGOFs, which act to deflect cracks and allow energy-consuming polymer deformation during yarn draw. Toughness was sensitive to the volume ratio of RGOFs to SWNTs in the spinning solution and the degree of graphene oxidation. The hybrid fibres were sewable and weavable, and could be shaped into high modulus springs.

Our US/Korea team described in Science that new electrochemical artificial muscles made of strong, tough, highly flexible yarns of carbon nanotubes can provide a thousand times higher rotation per length than previous artificial muscles. These muscles of helically-wound carbon nanotubes twist like the trunk of an elephant and accelerate a 2000 times heavier paddle up to
600 revolutions per minute within 1.4 s. Such torsional motion allows effective mixing of liquids on “micro-fluidic chips” used for chemical analysis and sensing. Unlike conventional motors, whose complexity makes them difficult to miniaturize, the torsional carbon nanotube muscles are simple to inexpensively construct in either very long or millimeter lengths.

In other NBIT supported work published in Science by the NBIT US/Korea team, we have designed guest-filled, twist-spun carbon nanotube yarns as electrolyte-free muscles that provide fast, high-force, large-stroke torsional and tensile actuation. Over a million reversible torsional and tensile actuation cycles are demonstrated, wherein a muscle spins a rotor at an average 11,500 revolutions/minute or delivers 3% tensile contraction at 1,200 cycles/minute. This rotation rate is 20 times higher than previously demonstrated for an artificial muscle and the 27.9 kW/kg power density during muscle contraction is 85 times higher than for natural skeletal muscle. Actuation of hybrid yarns by electrically, chemically, and photonically powered dimensional changes of yarn guest generates torsional rotation and contraction of the helical yarn host. Demonstrations include torsional motors, contractile muscles, and sensors that capture the energy of the sensing process to mechanically actuate.

NBIT co-sponsorship of the above discoveries on high performance artificial muscles is acknowledged in two patent applications8,9 filed in the United States, which will be combined as an international patent filing in August, 2013.

All of the below journal publications, except (1) and (4) are collaborative between US and Korea partners.

**NBIT II Publications and Patent Filings**


