

**Project Title: Energy Storage Based on Carbon Nanotube and Graphene**

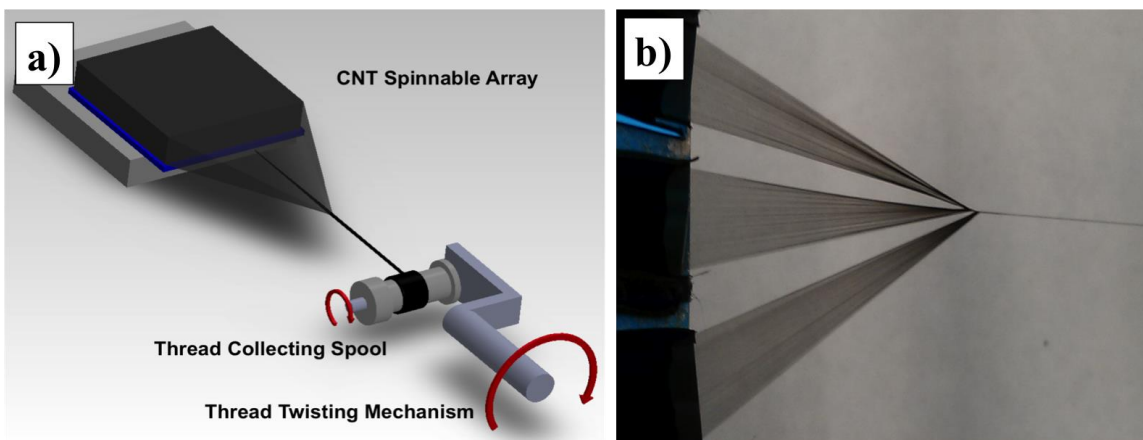
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**Project Context: Current Achievements at the UC Nanoworld Labs on Carbon Nanotube and Graphene Synthesis, Processing and Applications, including for Energy Storage.**

**1.1. Carbon Nanotube Fiber for Energy Storage.** The intrinsic physical properties of CNTs not seen in other materials, offer unique opportunities towards extraordinary technological applications [1,2]. CNT density is almost 1/10 of the most common electrically conducting metal-Cu, they are highly resistant to a broad range of acids and bases, which makes them ideal for electrodes [3]. The main benefit by applying CNTs in energy storage is the combination of the mechanical strength, electrical conductivity and large surface area of the CNTs. Although CNTs are still nanoscale materials, it is possible to assemble them into macroscale forms or assemblages such as continuous fibers and sheets. Today there are multiple fiber assembly methods: liquid phase, direct CVD and dry spinning from vertically aligned CNTs [4]. Dry spinning from vertically aligned process offers unique advantage compared to other methods. Assembling of catalyst free, aligned long CNTs into fibers, threads, films and sheets are among the main benefits. From a manufacturing point of view, the most promising advantage of the dry spinning processes is the ability to transfer CNTs onto macroscopic materials by preserving their pristine nature and without the use of additional manipulations or binders.

**1.2. Synthesis and Assembling.** CNT fiber dry spinning starts with the synthesis of vertically-aligned spinnable CNTs, typically about 400  $\mu\text{m}$  in length. Thin films of Fe and Co were used as catalyst source (total thickness of 1.2 nm) and they were sputtered on a 4 inch Si wafers that had a 5 nm  $\text{Al}_2\text{O}_3$  buffer layer, also deposited by sputtering. The Si substrates were loaded into a modified commercial CVD reactor ET3000 from CVD Equipment Corporation. The growth process took place at 740 Torr pressure. The reactor was heated to 400  $^\circ\text{C}$  for catalyst annealing under Ar, after 2 min. the reactor was ramped to 750  $^\circ\text{C}$ , and a 300 sccm mixture of  $\text{C}_2\text{H}_4$  and 1000 sccm of Ar were introduced at this temperature for 20 min. Upon growth completion, 30 sccm of  $\text{H}_2\text{O}$  and 2000 sccm of Ar were delivered during cooling to promote CNT array detachment. Detached spinnable CNT arrays have been assembled into a ribbon and simultaneously spun into a continuous fiber by a simple combination of twisting and drawing. Fig. 1a illustrates the process of draw-able CNT conversion into a fiber using a single array. Fig. 1b is a picture that shows three CNT arrays spun into a single fiber thus increasing the number of threads into the formed CNT fiber. Typically, CNT ribbon drawing starts at one edge of the array and continues until the CNT array is consumed at the opposite edge. The "glue" between the CNTs in the assemblages is only Van der Waals forces that hold together a continuous ribbon. Approximately each millimeter of CNT array allows drawing a meter long CNT ribbon [5,6]. Usually, the width of the array determines the amount of CNTs present in the thread, therefore it defines the diameter of a dry spun fiber. The CNT ribbons/sheets can be collected at a maximum linear speeds that reaches about 16 m/s [4]. More details of our current research on this topic are presented elsewhere [7,8,10,12] and are in alignment with other published results [9,11].



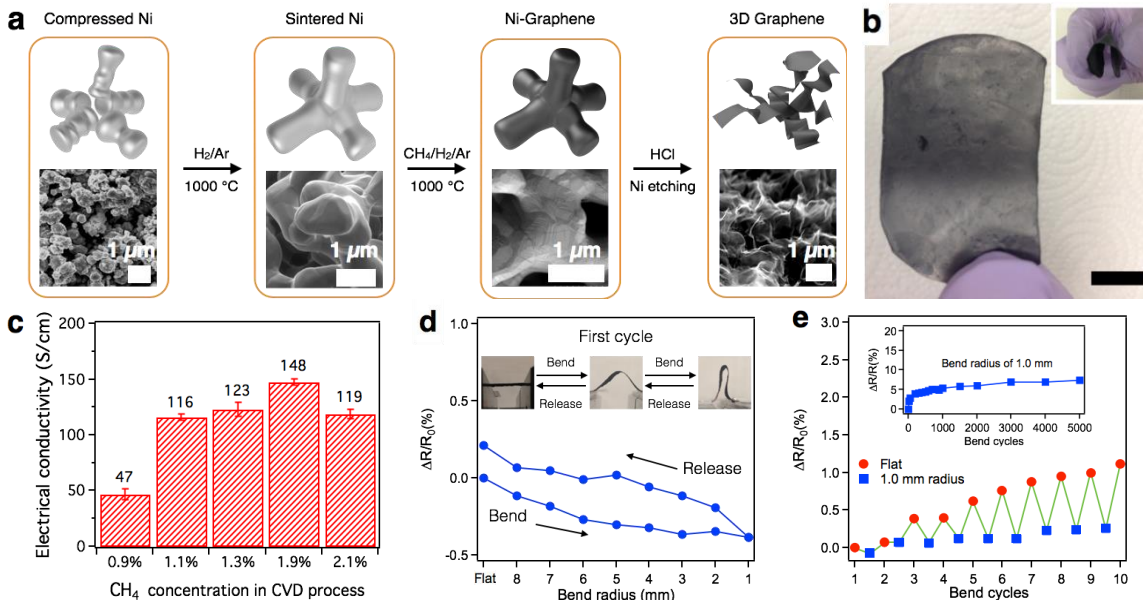
**Fig. 1.** Spinnable vertically aligned CNT assemble into a fiber, a) schematic representation of the CNT fiber spinning process, and b) picture of three CNT arrays spun into a single fiber.

**1.3. Synthesis and Assembling of Carbon Nanotube Sheet for Energy Storage.** Pulling single ribbons from vertically aligned CNT arrays and accumulating multiple layers results in producing CNT sheet. Fig. 2a illustrates the process of making CNT sheet to the required length and width. Formation of CNT sheet in real time is displayed in Fig. 2b, while Fig. 2c shows a picture of the 100 layer CNT sheet on a Teflon™ film that is used for the sheet support and handling. Typically volatile solvents such as ethanol, acetone, hexanes are used for densification and increase of the packing density of the CNTs within the sheet. Also, infrared (IR) heaters are placed under the CNT sheet to effectively dry the organic solvents



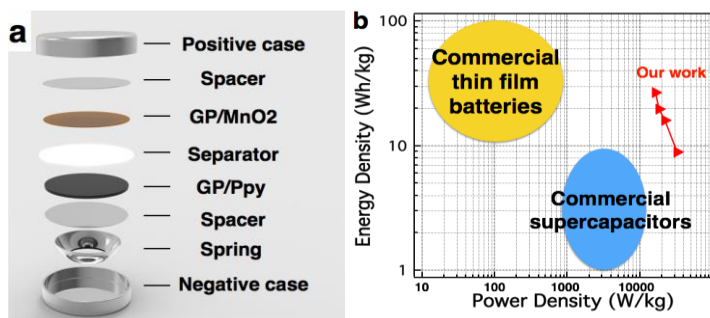
**Fig. 2.** CNT sheet assembly process: a) schematic representation; b) picture of CNT sheet fabricating process; c) picture of CNT sheet (100 layers) supported by a Teflon film.

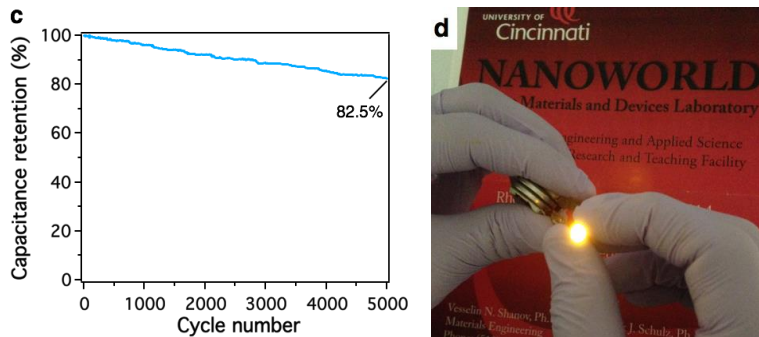
**1.4. Synthesis and Assembling of Graphene Paper for Energy Storage.** Bulk graphene and CNT materials are considered very promising renewable carbon electrode materials for energy storage devices. The graphene electrode materials created at Prof. Shanov' group is called graphene paper (GP). Details on its synthesis, properties and applications have been published recently [13]. Based on our patent pending approach [24], nickel powder with diameter of 2 to 3  $\mu\text{m}$  was pressed to form a nickel pellet and then sintered at 1000  $^{\circ}\text{C}$  under flow of argon to prevent oxidation. The pressing and heating steps enable sintering of the Ni powder through necking, which ultimately benefits the formation of a continuous and interconnected three-dimensional graphene structure during the sequential CVD process. As shown in Fig.3, graphene flakes have been integrated into a three-dimensional (3D) structure (Fig.3a and b) that exhibits good electrical conductivity of  $\sim 148 \text{ S/m}$ -(Fig.3c), and excellent electromechanical properties (only 7% increase in resistance after 5k bending-(Fig.3d and e). The GP also has a controlled pore size (2 nm) that allows good diffusion of electrolyte ions into the electrode structure. The described above good properties of GP make it as an ideal electrode material for energy storage applications.



**Fig. 3.** (a) GP synthesis by CVD; (b) Digital pictures of GP; (c) Electrical conductivity of GP as a function of the CH<sub>4</sub> concentration; (d) Resistance behavior of GP during 1 bending and releasing cycle; (e) Resistance retention of GP after 5,000 cycles.

**1.5. Device Fabrication and Testing.** The UC team has also explored the full device performance of GP by using GP/MnO<sub>2</sub> as positive electrode and GP/Polypyrrole (Ppy) as negative electrode. A coin cell supercapacitor (SC) prototype was assembled and studied (Fig.4a). The electrochemical test of the coin cell SC shows a maximum energy density of 26.7 Wh/kg at power density of 800 W/kg and a maximum power density of 8 kW/kg at an energy density of 9 Wh/kg. Our device outperforms many SCs reported in the literature [14-17]. The fabricated at UC supercapacitor surpasses also some commercial Li-ion batteries in terms of power density (~100 W/kg for Li-ion battery) and commercial SC in terms of energy density (~5 Wh/kg). The energy density and power density comparison that has been just described is shown in Fig.4b using a Ragone plot. The coin cell SC prototype also has a good cyclic life with 82.5% capacitance retention after 5,000 cyclic charge-discharge (CCD) at a high charge-discharge current of 10 A/g (Fig.4c). We also have demonstrated the ability of this SC prototype to power up different LEDs as shown in Fig.4d.





**Fig. 4.** (a) Illustration of GP/MnO<sub>2</sub>/Ppy coin cell SC assembly. (b) Ragone plot; (c) Capacitance retention of SC prototype after 5k CCD; (d) A two stacked GP/MnO<sub>2</sub>/Ppy SC prototypes powering an LED (3.0 V 30 mA).

**Project Description.** A general strategy to increase energy and power densities of electrochemical energy storage devices is through volume and mass reduction, while or improving their electrochemical performance. Microns thick, electrically conducting carbon nanotube (CNT) and graphene fibers and CNT ribbons or graphene paper, advanced at the UC Nanoworld Labs, are ideal supports for the electrode development due to their strength, flexibility and high electrical conductivity. Our goal is to assemble CNT and graphene based supercapacitors with both structural and energy storing functionalities in fiber and sheet format, and thin film batteries with energy and power densities that meet the requirements for aero-space applications.

**Facilities to be Used: Nanoworld at UC is One Stop Shop for Synthesis and Processing of Graphene and CNTs.** Nanoworld at UC offers a complete cycle from synthesis to fiber/sheet fabricating and application of CNT materials, including for energy storage. More details are published and patented elsewhere [13, 18-25]. Illustration of these capabilities along with making of different CNT assemblages is shown in Fig. 5. CNT thread can be sewed into fabric and the technology has been under development at UC for about five years. Increasing the strength of the thread is an objective in other research projects at UC. The properties of thread are being improved. Thread has strength of 1-2 GPa and strain to failure of 4% depending on the twist angle and diameter. The strain to failure of the thread can be tailored to the matrix material to achieve the combined strength of the two spinning at once; (d) drawing ribbon for functionalization; (d) CVD reactor ET3000 for growing spinnable arrays.



**Fig. 5.** Nanotube thread and sheet spinning and drawing at UC: (a) pristine 3D graphene; (b) ring spinning machine; (c) close-up of ring head invention at UC with four substrates spinning at once; (d) drawing ribbon for functionalization; (d) CVD reactor ET 3000 for growing spinnable arrays.

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