



A scalable nano-engineering method to synthesize 3D-graphene-carbon nanotube hybrid fibers for supercapacitor applications

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ABSTRACT

In this work, we describe a simple approach for the synthesis of three-dimensional graphene (3D-G) - carbon nanotube (CNT) hybrid fibers via Chemical Vapor Deposition (CVD). The obtained hybrid fiber was employed as a free-standing current collector in an electrochemical supercapacitor thus avoiding any conductive additives or metals. The amount of graphene synthesized on the CNT fiber and its properties have been easily tuned by different processing parameters, as described in the paper below. The fabricated fibers revealed a reasonable mechanical strength of 220.4 MPa and high electrical conductivity up to 649 Scm^{-1} . They also showed excellent electrochemical properties and capacitance that was important for their energy storage application. Interconnected PANI nanorods were grown on these fibers by oxidation polymerization, and the resulted fibrous hybrid structures were used as electrodes to make supercapacitors. The created devices employed an ionic liquid gel electrolyte (PVDF-EMIMBF₄) which had a voltage window of 3.2 V, thus increasing significantly the energy densities of the supercapacitors. The tested devices achieved a gravimetric energy density of 12.93 Wh/kg and a power density of 1350.25 W/kg at a current density of 1 A/g. They also demonstrated an areal energy density of $14.54 \mu\text{Wh/cm}^2$ and a power density of 1.37 mW/cm^2 at a current density of 1 mA/cm^2 .

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1. Introduction

In the field of energy storage, devices in fiber form are of great importance due to their potential use in medical implants, wearable electronics, and renewable energy [1–6]. In general, fibers have aesthetic significance, are mechanically flexible (especially for textiles) and lightweight, which makes them attractive for multiple high-tech applications.

Fiber-like energy storage materials made from metals showed some promising results due to their high electrical conductivities and superior strength [7,8]. Bae et al. [8] have reported a prototype of a high-efficiency supercapacitor using both flexible plastic wire and Kevlar wire on which ZnO nanowires were grown by hydrothermal method. Their electrodes have been synthesized at low

temperatures (less than 100°C) and were biocompatible and environmentally friendly [8]. However, they revealed weak interfacial properties which limited their use in supercapacitor applications [9–11].

Graphene has been used to improve the X-ray photon response in solution-synthesized CsPbBr₃ nanoparticles [12], for efficient removal of rhodamine B and other dyes [13], and in in-vivo bioimaging as a GO-AgInZnS photoluminescent and water-soluble composite [14]. These and other applications were possible because of the extraordinary properties of graphene including its low density, high electrical conductivity, large surface area, high mechanical, thermal and chemical stability, as well as large electron mobility [15–19]. Due to these remarkable qualities, different graphene forms have been reported, including 1-D fibers, 2-D thin films and 3-D structures for multiple technical applications [20–25]. Graphene-based materials have also emerged as promising candidates for energy storage applications.

There have been several publications on the synthesis and

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fabrication of graphene fibers [22,25–28]. A few groups employed wet spinning of graphene oxide liquid crystals forming graphene fiber in coagulation baths of NaOH or methanol, and subsequently reducing them in hydriodic acid [28–30]. Xu et al. extruded graphene oxide liquid crystals into liquid nitrogen and then freeze-dried them to form graphene aerogel fiber [31]. Dimension-confined hydrothermal strategy has also been applied to aqueous graphene oxide suspensions to create graphene fiber by Hu et al. [32]. They reduced and spontaneously assembled graphene oxide into a fibrous shape material and post-processed them by etching or by other chemistry converting them into graphene fibers [33]. The approaches starting with graphene oxide, however, create graphene fibers with weak bonding and thus reveal lower mechanical strengths and electrical conductivity compared to graphene assemblies that have covalently bonded graphene sheets.

Another promising carbon material for fiber-like energy storage applications is CNTs and their assemblies. Due to their ability to be spun [34], CNTs are widely studied and used for fabricating fiber shaped carbon derivatives. They have high mechanical strength, low density, great chemical resistance and electrical conductivity [35,36].

Several groups have used CNTs and related hybrids for yarn supercapacitors and battery applications [6,23,37–41]. Chen et al. for example fabricated an electric double layer capacitor (EDLC) consisted of aligned CNT fiber and a CNT sheet, both functionalized as two electrodes and assembled with a polymer gel sandwiched between them [40]. Ren et al. also developed wire shaped micro-supercapacitors and micro-batteries using multi-walled CNTs by twisting the fibers to form supercapacitors [38]. The reported CNT based energy storage devices revealed promising results, however, one of the main challenges in applying CNT assemblages in energy storage applications is the reduction of their surface area during their fabrication. The reduced surface area has an adverse effect on the electrochemical performance of the CNT-based electrodes such as limited space for loading active materials and poor electrolyte diffusion.

Integration of graphene and CNT holds promise for making a hybrid material that can enable fiber-like energy storage applications. For example, Cheng et al. [23] reported the synthesis of CNT on graphene fibers and their possible applications in energy storage. However, the graphene fiber on which their CNTs were grown was made by using graphene oxide suspension and a hydrothermal process. This method, therefore, yielded a significantly lower material capacitance and mechanical strength due to the weak bonds between graphene and CNTs. Alternatively, using CNT fibers as core materials and functionalizing them by chemical coating and doping, showed potential to develop a high strength fiber-like energy storage system, while ensuring high specific surface area, as well as the good electrochemical activity [41–43].

In this work, we report a simple, scalable and practical method to nano-engineer CNT fibers and to create a three-dimensional graphene-CNT hybrid fiber (3DGCNT). The materials' processing approach was based on continuous coating of the CNT fibers with a nickel catalyst followed by subsequent growth of 3-D graphene flakes within the fiber by Chemical Vapor Deposition (CVD). The obtained hybrid material leverages the unique properties of both graphene and CNTs. The polymer PANI, due to its high electronic conductivity, redox and ion exchange properties, and environmental stability, has been used widely in the fabrication of supercapacitors [44–46]. Therefore, the fabricated fiber (3DGCNT) was further decorated with polyaniline (PANI) nanorods by a chemical oxidative polymerization method [43,44] and studied to explore its potential applications for high energy density supercapacitors. As described below, devices formed in this work from the PANI-Graphene-CNT hybrid fibers revealed superior electrochemical

performance due to the fast-redox reactions between the PANI and the electrolyte used.

2. Experimental

2.1. Fabrication of Graphene-CNT hybrid fiber

A CNT fiber was dry spun from CNT arrays which had been synthesized by Chemical Vapor Deposition [34]. The CNT fiber was then passed through a Ni catalyst slurry as shown in Fig. 1. The catalyst slurry was made up of a mixture of polystyrene (PS), diethylene-glycol-dibenzanoate (DEGDB) as a plasticizer, and Ni powder (3–7 μm size) with varying amounts of toluene solvent. The resulting Ni concentrations in the used slurries were 3.3 g/ml, 2.5 g/ml and 2 g/ml, respectively depending on the solvent amount. The PS served as a binder for the Ni particles, which helped to maintain the sintering of the nickel particles during the annealing step in the CVD reactor. DEGDB acted as a plasticizer reducing brittleness and promoting flexibility after the slurry dries out on the surface of the fiber. The solvent toluene in the slurry dissolves the PS and densifies the fiber. It was found that the thicker the solution (less amount of toluene) the more significant the amount of graphene grown on the fibers. This was ascribed to a thicker coating of Ni, which was the catalyst for graphene growth on the surface of the fiber. A temperature-time profile used in the CVD growth process of 3D-G-CNT is displayed in Fig. S1.

The sintering process in the CVD reactor is essential to create the nickel scaffold within which the carbon atoms from the methane precursor dissolved at 1000 $^{\circ}\text{C}$ and further formed 3D-Graphene. The CNT fiber accommodated Ni particles on its surface, which after the graphene formation have been etched out using hydrochloric (HCl) acid. Details regarding the CVD process are described in our previous publications [21,47].

As seen in Fig. 1, our set-up consists of a motor, which moves the CNT fiber through a catalyst slurry at a constant speed. This system yields a highly uniform coating of the catalyst particles on the CNT fiber. The collected fiber is then transferred into a CVD furnace for graphene synthesis. The final 3DGCNT fiber was derived by etching out nickel from the CNT-graphene/nickel fiber in an acid bath containing equal portions of HCl and water at 80 $^{\circ}\text{C}$ for 10 h. The obtained 3DGCNT was rinsed with DI water to remove residual acid and then dried out in direct air. We refer here the 3DGCNT fibers by the concentration of Ni used in the slurry for their fabrication such as: 3.3gml⁻¹-3DGCNT, 2.5gml⁻¹-3DGCNT, and 2gml⁻¹-3DGCNT, respectively.

2.2. Electrode fabrication

All electrodes and devices were made using 7.5 cm long fibers. These fibers were attached to copper tapes with fast drying silver paint (TedPella Inc.). The copper tape served as an electrically conducting lead to the electrochemical analysis arrangement. In the fabricated device, the electrodes were coated with a gel electrolyte comprising of polyvinylidene fluoride-co-hexafluoropropylene and 1-ethyl-3-methylimidazolium (PVDF-EMIMBF₄) and after curing, were placed parallel to each other on a cellulose weighing paper (LabExact). The gel electrolyte was added to this configuration of fibers and sealed with a Kapton tape to create a device.

2.3. Fabrication of the PANI-graphene-CNT hybrid

To prepare the PANI-3D-Graphene-CNT (PANI-3DGCNT) fiber, we used the 2.5gml⁻¹-3DGCNT electrodes and placed them in a beaker with 1 M aniline monomer dissolved in 1 mol/L HCl and 1 M ammonium peroxydisulphate (APS) in 1 mol/L HCl, as reported in

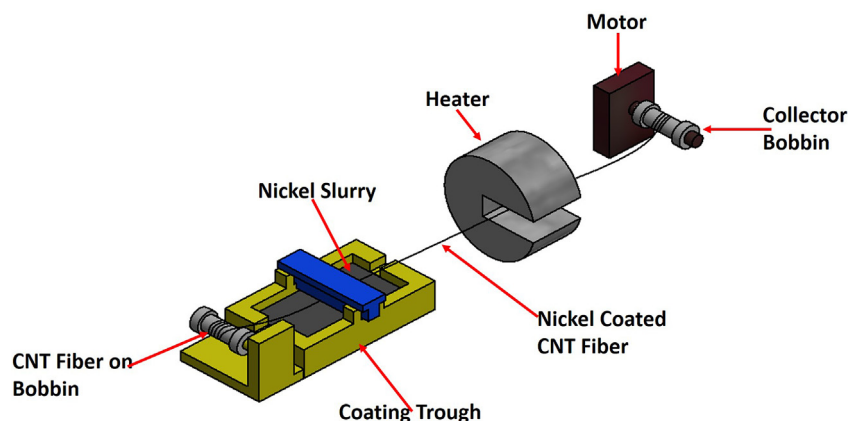


Fig. 1. Schematic of the continuous Ni catalyst coating set-up on CNT spun fiber.

our previous work [43]. The hybrid fiber was created at a 2:1 ratio (aniline monomer to APS) over an hour. The PANI formed on the fiber and was characterized by Raman spectroscopy, FTIR and SEM. The as-prepared hybrid fiber was rinsed in DI water and used to create devices.

2.4. Characterization of the CNT fibers

Scanning electron microscopy (SEM) (FEI SCIOS dual beam, 5 kV) and Surface Enhanced Raman Spectroscopy (SERS) using a custom Nikon Ti Eclipse inverted dark-field microscope with a Nikon darkfield condenser (Ni-E 0.95–0.8) [48], have been conducted. Raman spectroscopy (Renishaw inVia, equipped with 514 nm Ar-ion laser and a laser spot of $\sim 1 \mu\text{m}^2$) was also used to characterize the synthesized PANI-based electrodes. TEM imaging was conducted with a Philips CM-20 TEM system, specific surface area and pore volumes of outgassed samples were obtained using a Micromeritics ASAP 2060 accelerated surface area and porosity measurement system via nitrogen adsorption at -196.052°C . A Nicolet 6700 FTIR spectrophotometer was employed to collect FTIR data.

Resistivity measurements were derived using a four-probe method. The tensile strength of the fiber was evaluated by with a Micro Instron Testing Machine Model 5948 with pneumatic grippers, Instron, Norwood MA. An active gauge length of 23 mm and a strain rate of 1 mm/min were used during this testing.

Electrochemical measurements were carried out for the fibers with a Gamry, Interface 1000 electrochemical workstation at room temperature. Graphene-CNT fiber and CNT fiber underwent cyclic voltammetry, galvanostatic charge-discharge, and electrochemical impedance spectroscopy measurements over a frequency range from 10^5 to 10^{-1} Hz at a sinusoidal voltage amplitude of 10 mV and an open circuit potential. The capacitance (C) of the devices and of the electrodes was calculated using equation $C = I\Delta t/\Delta V$. The gravimetric capacitance (C_m), the areal capacitance (C_A) and volumetric capacitance (C_V) were calculated by the following formula: $C_m = C_{\text{device}}/m$, $C_A = C_{\text{device}}/A$ and $C_V = C_{\text{device}}/V$, respectively. The gravimetric energy density (E_m) and power density (P_m) were calculated by the equations: $E_m = \frac{1}{2} * \frac{C_m(\Delta V)^2}{3.6}$ and $P_m = 3600 \frac{E_m}{t}$. The areal energy density (E_A) and power density (P_A) were computed by the expressions: $E_A = \frac{1}{2} * \frac{C_A(\Delta V)^2}{3.6}$ and $P_A = 3600 \frac{E_A}{t}$. The volumetric energy density (E_V) and power density (P_V) were calculated by the equations: $E_V = \frac{1}{2} * \frac{C_V(\Delta V)^2}{3.6}$ and $P_V = 3600 \frac{E_V}{t}$, where I is the discharge current, t is the discharge time, ΔV is the operating

voltage window, m , A and V refer to the mass, area and volume of the device, respectively [43,49–51].

3. Results and discussion

3.1. Characterization of 3DGCNT hybrid fibers

3.1.1. Electrical conductivity and tensile strength

Resistivity and conductivity measurements for our 3DGCNT fibers have been obtained by a four-probe set-up. This data has been compared with the conductivity of pristine CNT fibers. It was observed that there was a dramatic increase in conductivity values for the 3DGCNT fibers over pristine CNT samples (Fig. 2a), which was attributed to the presence of graphene on the fibers, as well as to their densification by toluene (Fig. S2). During the Ni catalyst coating process, the fibers were densified by the toluene solvent. Capillary forces, therefore, acted upon the individual CNTs and bundles within the fiber bringing the tubes closer, thus increasing the overall electrical conductivity. This densification process explains why the 2gml^{-1} -3DGCNT revealed a higher conductivity over the 3.3gml^{-1} -3DGCNT even though the 3.3gml^{-1} -3DGCNT had more graphene on its surface.

Fig. 2b presents tensile test data comparing the 3DGCNT to pristine CNT fibers. It is apparent from the data that the strength of the processed fibers decreased due to damages and defects generated during the synthesis process. It was also noticed that the CNT fiber served as a carbon source for the growth of graphene, which is described in detail in the “SEM Study” section below. The 3.3gml^{-1} -3DGCNT fiber was the most brittle of all samples, however with the most graphene grown on it, as observed in the same SEM section. It is reasonable to believe that part of the core CNT fiber has been consumed during the CVD process thus decreasing the overall strength and increasing the brittleness of the resulted hybrid material.

Table 1 below presents a comparison of our data for 3DGCNT fibers with literature data for graphene and graphene-based hybrid fibers in terms of electrical conductivity and tensile strength. From this Table, it is evident that our fibers are highly conductive and competitive in terms of strength when compared to published data for similar fibers.

3.1.2. Raman spectroscopy

Raman data was acquired for the D-CNT and 3DGCNT samples. A typical Raman spectrum of a graphitic material has three peaks: D, G, and 2D at 1350 cm^{-1} , 1585 cm^{-1} , and 2700 cm^{-1} , respectively.

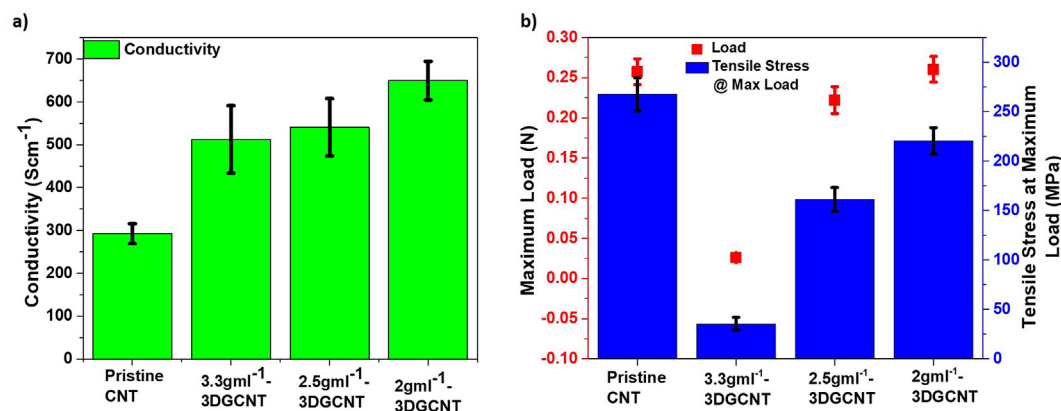


Fig. 2. Comparison of properties of CNT fiber processed at different conditions: a) Electrical conductivity of the fibers; b) Maximum load and corresponding tensile stress of the fibers.

Table 1

Literature data comparison of strength and electrical conductivities of graphene and graphene-based hybrid fibers with data from this work.

Method	Diameter (μm)	Strength (Mpa)	Conductivity (Scm^{-1})	Reference
Wet spinning GO	25–120	145	35 ^a	[52]
	40–150	85–192	68–230 ^a	[53]
	<100	442 $\pm$ 18	28.44 ^b	[30]
Wet spinning GO + dip coating (SGO)	~115	—	40	[54]
Wet spinning RGO-PEDOT:PSS	~100	18.4	590	[55]
Wet spinning + Ionic bonding and π - π interaction with PSE-AP	—	740.1	384.3	[56]
Non-liquid crystal spinning of GO-CNC	—	199.8	64.7	[57]
Spinning of GONR	29–80	33.2, 383 ^b	285 ^b	[22]
Hydrothermal process	10–100	140	~10	[20]
CVD assisted	20–50	—	~10	[58]
Spontaneous reduction and assembly of GO	15–100	—	~10	[33]
Aligned CNT to graphene yarn	~100	—	100 $\text{Scm}^2\text{g}^{-1}$ ^b	[27]
3.3gml ⁻¹ -3DGCNT	40–50	35.5	512.6	This work
2.5gml ⁻¹ -3DGCNT	40–50	161.07	540.85	This work
2gml ⁻¹ -3DGCNT	40–50	220.36	649.72	This work

^aAfter chemical reduction ^a

^bAfter annealing at high-temperature ^b

The D band reveals defects in the material due to the formation of sp^3 bonds or single-bonded carbons on its surface. The G band is indicative of sp^2 hybridized carbon atoms with double bonds, whilst the 2D band originates from the second order-double resonant Raman scattering from zone boundary phonons [59–62]. A semi-quantitative evaluation of the created defects can be obtained from the intensities (I_D/I_G) ratios.

In Fig. 3a and b are presented Raman spectra of the 2.5gml⁻¹-3DGCNT fibers. It has been observed there that on the spectra of the 2.5gml⁻¹-3DGCNT fiber, there were three main zones with varying I_D/I_G ratios. Fig. 3a displays an SEM image of the 2.5gml⁻¹-3DGCNT fiber along with Raman spectra obtained from different regions of its surface. We classify these regions as defect-rich CNTs, pristine CNTs, and pure graphene. They are randomly distributed on the surface of the fibers. The defect-rich regions are areas where the CNT bundles and tubes within the bundles have been altered during the CVD process. These regions typically show greater I_D/I_G ratios [63], while the pristine regions were not affected adversely during the CVD process. The I_D/I_G ratio of D-CNT (Fig. 3c) is approximately the same as that seen in the pristine region of the 2.5gml⁻¹-3DGCNT fiber (0.69), confirming that those regions were unaffected by the CVD process. The graphene-rich regions are found where graphene grows in bulk on the surface of the fiber, thus showing a very low I_D/I_G ratios, which is typical for pure graphene [64]. Raman spectra have been used to identify single, bi and few-layer graphene [60,62,65,66] by obtaining the I_G/I_{2D} ratios.

From Fig. S3 one can conclude that the formed 3D graphene was multi-layered with an I_G/I_{2D} ratio of 2.14. This is consistent with data from our previous work [47].

In Fig. 3d is displayed the Raman spectra of the PANI-3DGCNT along with pristine CNT and pure PANI. The PANI characteristic peaks on the PANI-3DGCNT fiber proved the successful synthesis of this polymer on the surface of the fiber. The peak at 1168 cm^{-1} represents the in-plane deformation of the C–C bond of the quinoid rings, while those at 1349 cm^{-1} and 1498 cm^{-1} represent the C–N and C=N stretching in quinoid and benzenoid rings, respectively [67,68]. Fig. 3e shows the FTIR spectra of the synthesized PANI. The FTIR spectra exhibit the ring stretching vibrations of the benzenoid and quinoid rings of aniline at 1500 cm^{-1} and 1600 cm^{-1} , respectively [69] thus proving the presence of PANI on the CNT fibers.

3.1.3. Structural characterization of 3DGCNT and PANI-3DGCNT fibers

SEM images were taken from the three 3DGCNT fibers (3.3gml⁻¹-3DGCNT, 2.5gml⁻¹-3DGCNT, and 2gml⁻¹-3DGCNT), and from the PANI-3DGCNT synthesized fibers. It was observed that the lesser the amount of toluene used in the Ni slurry, the more substantial the amount of graphene grown on the fiber. From Fig. 4a and d, it can be concluded that CNTs are hardly seen on the surface of the 3.3gml⁻¹-3DGCNT fiber. This fiber seems entirely encapsulated in graphene. A possible explanation is that the 3.3 g/ml Ni slurry was denser than the others, leading to a greater Ni coating on

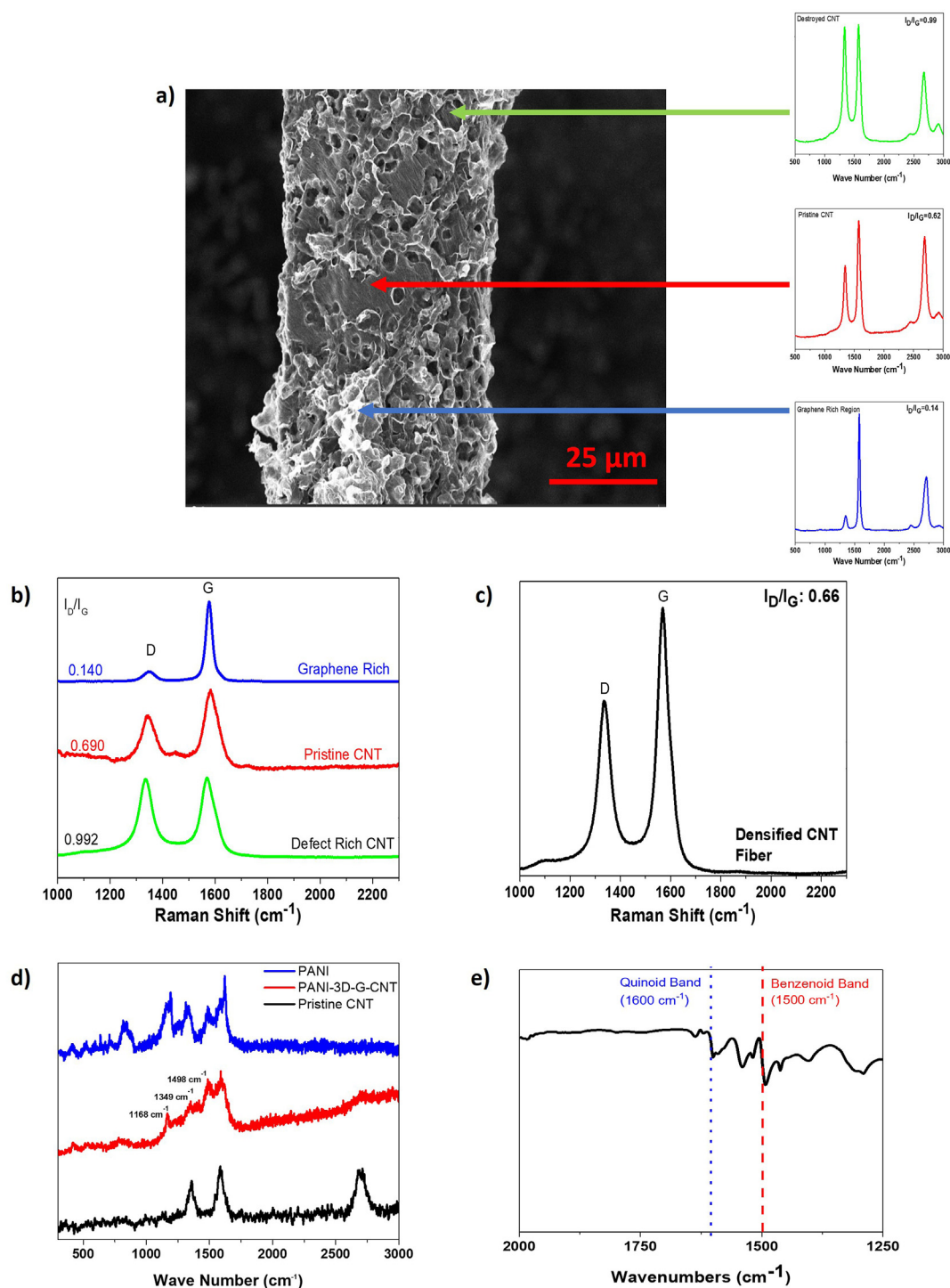


Fig. 3. Raman spectra of: a) 3DGCNT fiber showing various regions on its surface; b) Enlarged image of spectra of various regions in a); c) Pristine CNT; d) Raman spectra showing pristine CNT, PANI-3DGCNT, and pure PANI; e) FTIR of synthesized PANI showing benzenoid and quinoid bands.

the surface of the fiber and subsequently a higher mass of grown graphene during the CVD process.

From the images of the 2.5gml⁻¹-3DGCNT fiber, shown in Fig. 4b and e, it was observed that the growth of graphene occurred at select areas, while there were a few spots on the surface of the fiber where the texture of the CNT bundles was seen. Here, one can conclude that the CNT fiber used to make the 2.5gml⁻¹-3DGCNT hybrid material was not uniformly coated with Ni slurry, which led to the growth of graphene in patches on its surface.

In Fig. 4c and f, SEM images of the 2gml⁻¹-3DGCNT fiber are presented. It was obvious that there was not much growth of graphene on this fiber when compared with the 2.5gml⁻¹-3DGCNT and 3.3gml⁻¹-3DGCNT, respectively. From Fig. 4f however, it is seen that the growth of graphene flakes occurred in the formed pores within the CNT fibers. A simple explanation for this phenomenon is that the Ni particles stuck on the CNT fiber started consuming carbon from the CNTs thus digging within the fiber (Fig. S4). Therefore, graphene was formed within the created cavities during

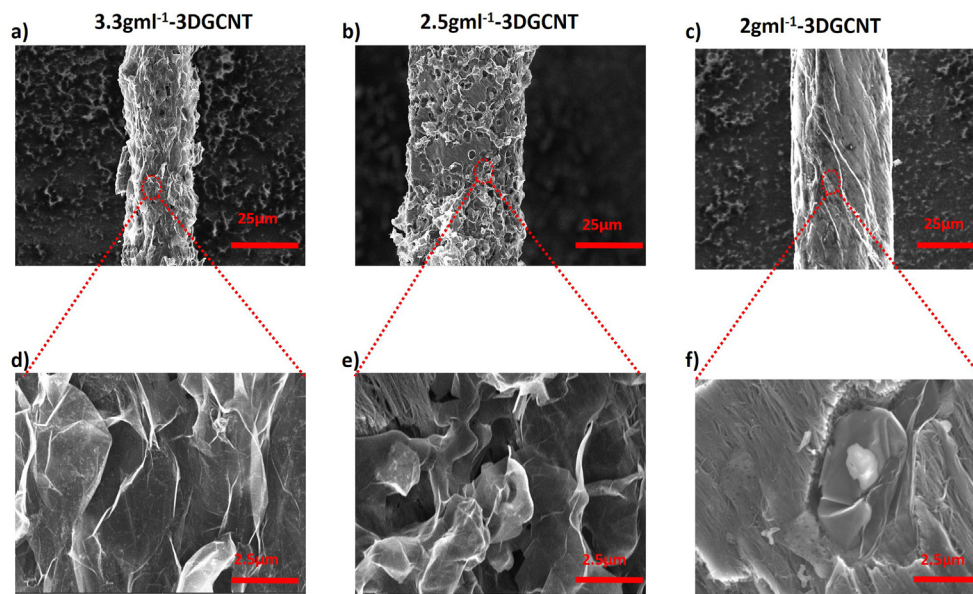


Fig. 4. SEM images of 3DGCNT fibers: a) 3DGCNT fiber made from 3.3 g/ml Ni slurry; b) 3DGCNT fiber made from 2.5 g/ml Ni slurry; c) 3D-G-CNT fiber made from 2 g/ml Ni slurry; d) Enlarged image of Figure 4a); e) Enlarged image of Figure 4b); f) Enlarged image of Figure 4c).

the CVD process. This affected negatively the tensile strength of the fiber as shown earlier in Fig. 2b. This loss in strength can be credited to the consumption of carbon from the CNTs within the fiber during the CVD process.

The 2.5 g ml⁻¹-3DGCNT fiber was sonicated in 5 ml isopropyl alcohol for 10 min, and the resulting suspension was dropped onto lacy carbon – copper grids for TEM analysis. The TEM image in Fig. 5a clearly shows the presence of graphene and CNT bundles which have been further identified by selected area electron diffraction (SAED), as displayed in Fig. 5b and c. The graphene SAED pattern allowed to obtain a lattice spacing value of ~0.21 nm, which corresponds to the (1100) lattice fringe [70–72]. The image of graphene in Fig. 5a revealed a thin, flat and crumpled flake where the central part was clear and without much features, while the edge was scrolled and crumpled up. This morphology has been described and explained in the literature as intrinsic to graphene [73,74].

To investigate the cross-sectional area of the composite CNT fiber and eventual presence of graphene in the core of the fiber, a

2.5 g ml⁻¹-3DGCNT sample was cut by Focused Ion Beam (FIB). The resulting SEM images are presented in Fig. 6. The cut went across graphene flakes located on the surface of the fiber (Fig. 6a and c) and through the fiber itself. Fig. 6b and d presented the cross-section of the fiber, where no graphene was found in its bulk. This confirmed that the synthesis process employed in this work affected only the fiber's surface without any nickel catalyst penetration within the core of the CNT fiber.

Fig. 7a and b displays SEM images of the PANI-3DGCNT fiber. Interconnected PANI nanorods with graphene flakes have been observed on the surface of the CNT fiber. In this case, the 3DGCNT fiber served as an excellent nanostructured template accommodating the deposition of PANI.

BET specific surface area measurements have been conducted via nitrogen adsorption at –196.052 °C, which yielded the isotherms displayed in Fig. S5. The obtained results are presented in Table 2. It is apparent from the data there that the 3DGCNT fibers possessed about double the specific surface area of the toluene densified fiber. The 2.5 g ml⁻¹-3DGCNT fiber revealed larger

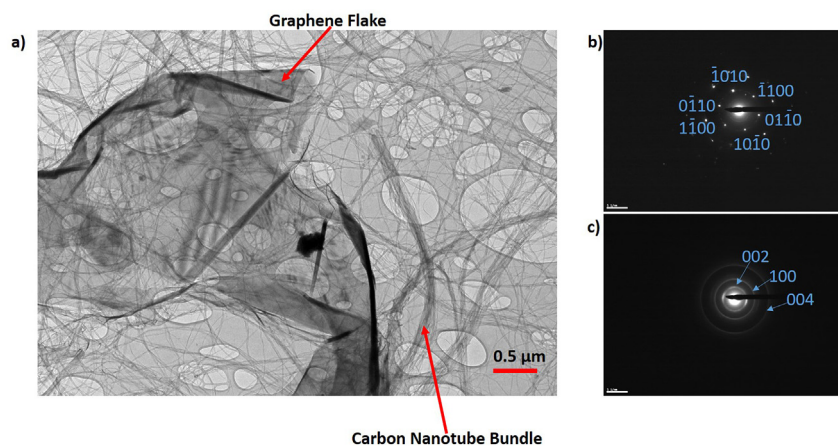


Fig. 5. a) TEM micrograph of graphene flake and carbon nanotubes obtained from the 3DGCNT fiber; b) SAED pattern of a graphene flake; c) SAED pattern of carbon nanotube bundle. The scalebar in Figures 5b and c is 5 nm.

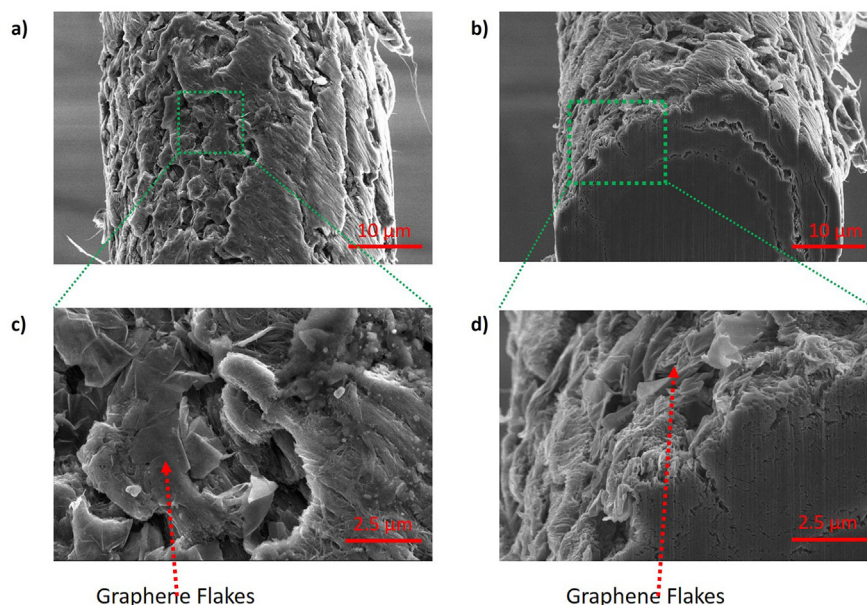


Fig. 6. SEM image of a) 2.5 g ml^{-1} -3DGCNT at 2500X; b) FIB cut edge of 2.5 g ml^{-1} -3DGCNT fiber at 2500X; c) Higher magnification image (25000X) of the fiber's surface showing graphene flakes along with CNTs; d) Cross-sectional edge image of the of 2.5 g ml^{-1} -3DGCNT fiber at 25000X.

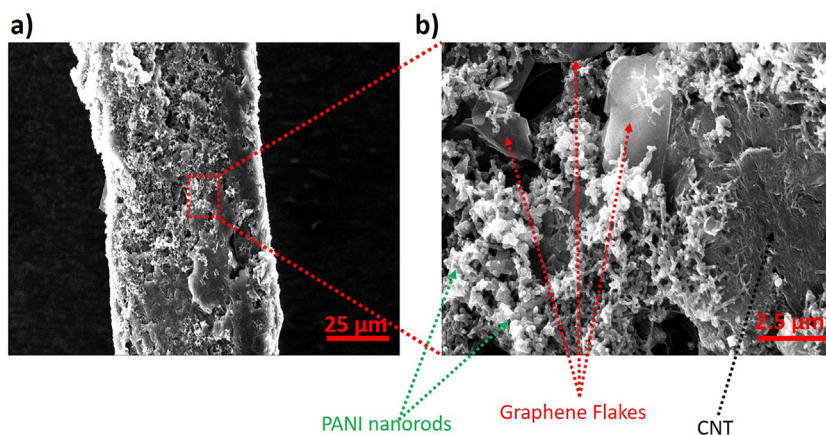


Fig. 7. a) SEM image of PANI-3DGCNT fiber; b) Enlarged image of Figure 7a highlighting PANI nanorods, graphene flakes, and CNTs.

Table 2
BET specific surface area measurements of the tested CNT hybrid fibers.

Sample	Specific surface area (m^2/g)	Standard error (m^2/g)
Toluene Densified CNT	51.97	0.4480
2 g ml^{-1} -3DGCNT	105.81	0.2134
2.5 g ml^{-1} -3DGCNT	121.28	0.1925

specific surface area than the 2 g ml^{-1} -3DGCNT sample, which is attributed to the fact that there was more graphene on that fiber's surface as seen in the SEM images, and graphene theoretically has a larger specific surface area than CNTs [75].

3.1.4. Electrochemical performance evaluation of the 3DGCNT hybrid fibers

Three-electrode tests were run for the pristine, densified and 3DGCNT fibers. The electrodes were fabricated using 7.5 cm long portions of the fibers. The tailored samples were attached to copper tapes with fast drying silver paint. The copper tapes served as leads

to be connected to the electrochemical testing stations. The 3.3 g ml^{-1} -3DGCNT fiber could not be tested due to its extreme brittleness and difficulty to handle. Ag/AgCl served as a reference, the platinum wire was used as a counter, and Na_2SO_4 was the electrolyte of choice in this test.

Cyclic voltammetry (200 mV/s) and charge-discharge data (1 A/g) from the prepared electrodes are presented in Fig. 8a and b, respectively. From these graphs, one can notice that the 2.5 g ml^{-1} -3DGCNT fiber electrode demonstrated the best electrochemical data including larger cyclic voltammetry curve, as well as the more extended duration shown in its galvanostatic charge-discharge test. This improved electrochemical performance is attributed to the larger surface area of the electrode as shown in the in Table 2. The data there for the 2.5 g ml^{-1} -3DGCNT sample showed a value of $121.28 \pm 0.1925\text{ m}^2/\text{g}$ compared to the 2 g ml^{-1} -3DGCNT ($105.81 \pm 0.2134\text{ m}^2/\text{g}$), and the toluene densified CNT fiber ($51.97 \pm 0.4480\text{ m}^2/\text{g}$). The surface area of the electrode is directly proportional to its capacitance. This is obvious from the equation $C = S\epsilon/d$, where C is the capacitance, S is the electrode surface area,

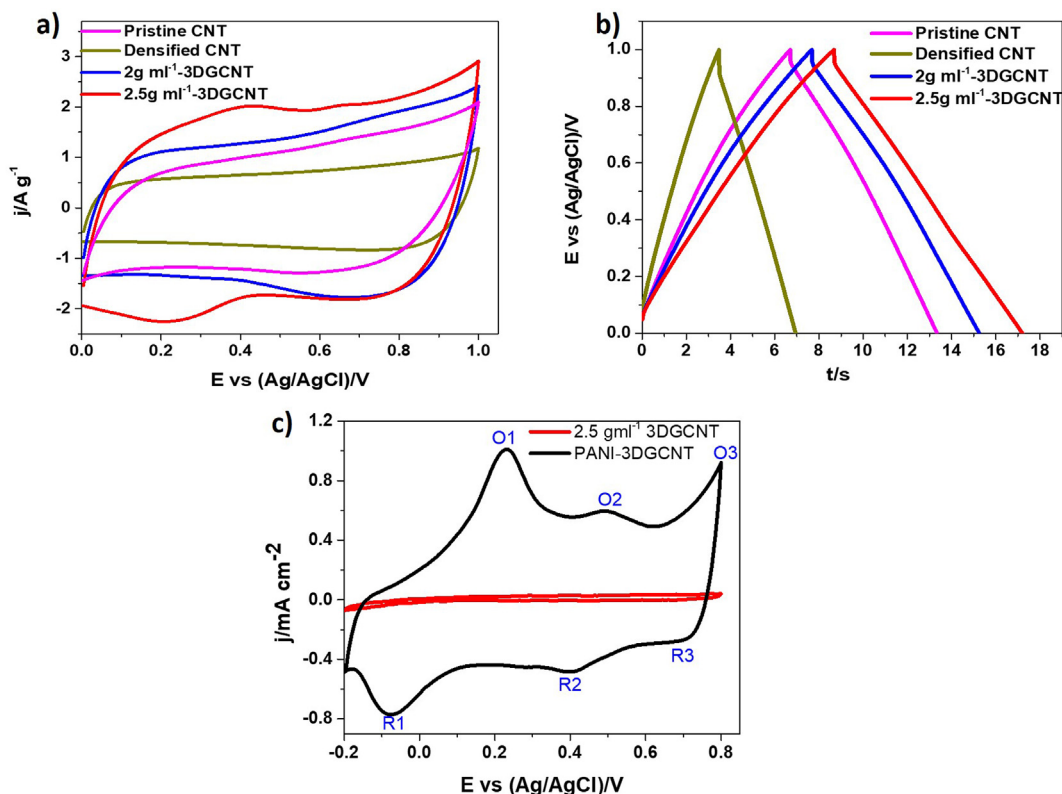


Fig. 8. a) Cyclic Voltammetry of fabricated fibers at 200mV/s; b) Charge-Discharge of the fibers at 1 A/g; c) Half Cell Test at 5mV/s of PANI-3DGCNT and 2.5g ml⁻¹-3DGCNT.

ϵ is relative permittivity of the solution (medium) and d is the thickness of the double layer [76].

Due to its superior electrochemical performance and high surface area, the 2.5g ml⁻¹-3DGCNT fiber was selected to serve as a scaffold for the PANI deposition and to fabricate a full supercapacitor device. From the charge-discharge graph (Fig. 8b), we note that the densified fiber had the worst capacitance. During the densifying process, capillary forces act on the individual nanotubes and related bundles causing the fibers to contract, thus altering their properties such as surface area and porosity. The latter affected adversely the capacitance of the densified fiber.

Fig. 8c compares CV curves of 2.5g ml⁻¹-3DGCNT and PANI-3DGCNT at 5 mV/s in 1 M H₂SO₄. It was observed that the pseudocapacitive material PANI on the surface of the PANI-3DGCNT participated in fast surface and near-surface redox reactions and therefore contributed to a better electrochemical performance. This is consistent with what is reported in the literature from PANI in similar applications [77–79]. As shown in this work, PANI decorated fiber revealed better electrochemical performance illustrated by the larger area CV curve. Further, it was noticed that the PANI decorated fiber exposed three oxidation and reduction peaks labeled as O1/R1, O2/R2 and O3/R3, which corresponded well with the redox reactions taking place. O1/R1 represents the redox transition of leucoemeraldine/emeraldine forms, O2/R2 denotes the hydroquinone/benzoquinone redox reaction, whilst the O3/R3 represent the faradaic transformation of emeraldine/pernigraniline forms [80–82]. It is reasonable to believe that the observed redox reactions are responsible for the improved capacitance of the PANI decorated fiber.

We fabricate fiber supercapacitors from the electrode with the best electrochemical performance (2.5gml⁻¹-3DGCNT). We also used it as a template for PANI deposition thereby creating fiber supercapacitors from 2.5gml⁻¹-3DGCNT and PANI-3DGCNT with

PVDF-EMIMBF₄ as an electrolyte. Fig. 9a presents cyclic voltammetry curves at 200 mV/s for both 2.5gml⁻¹-3DGCNT and PANI-3DGCNT fiber supercapacitor devices. The PANI-3DGCNT device revealed better electrochemical behavior compared to the fiber electrode device that was not decorated with the polymer. This conclusion was supported by the observed large area under the Cyclic Voltammetry curve compared to that of 2.5gml⁻¹-3DGCNT. At a current density of 1 mA/cm², the PANI-3DGCNT device showed an energy density of 14.54 μ Wh/cm² and a power density of 1.37 mW/cm², while the 2.5gml⁻¹-3DGCNT device revealed more modest data such as energy density of 7.28 μ Wh/cm² and a power density of 1.31 mW/cm².

The galvanostatic charge-discharge behavior of the fiber devices is shown in Fig. 9b. The graphs represented there were obtained at a current density of 2 mA/cm². It was observed a longer time to charge which was attributed to the increased diffusion resistance of the electrolyte ions. Such a behavior was found only at lower scan rates (Fig. S6). From the same graphs, it was noted that the PANI-3DGCNT device revealed a higher discharge time leading to a larger capacitance than that of the 2.5gml⁻¹-3DGCNT.

The Nyquist plot comparison for the two devices is shown in Fig. 9c. The equivalent series resistance (ESR) was estimated at the point at which the graphs intersected with the X-axis. It determined the internal resistance which appeared in series with the device [83]. The PANI-3DGCNT device showed a far lower ESR than the 2.5gml⁻¹-3DGCNT. This caused a better ion charge transfer in the PANI-3DGCNT device compared with the 2.5gml⁻¹-3DGCNT one, which contributed to the achieved excellent energy density.

Fig. 9d represents a Ragone plot and compares the energy and power densities of the fabricated EMIMBF₄ devices with other fiber supercapacitors reported in the literature. As shown there, our supercapacitors revealed superior energy densities and excellent power densities. In the case of the PANI based device, one can

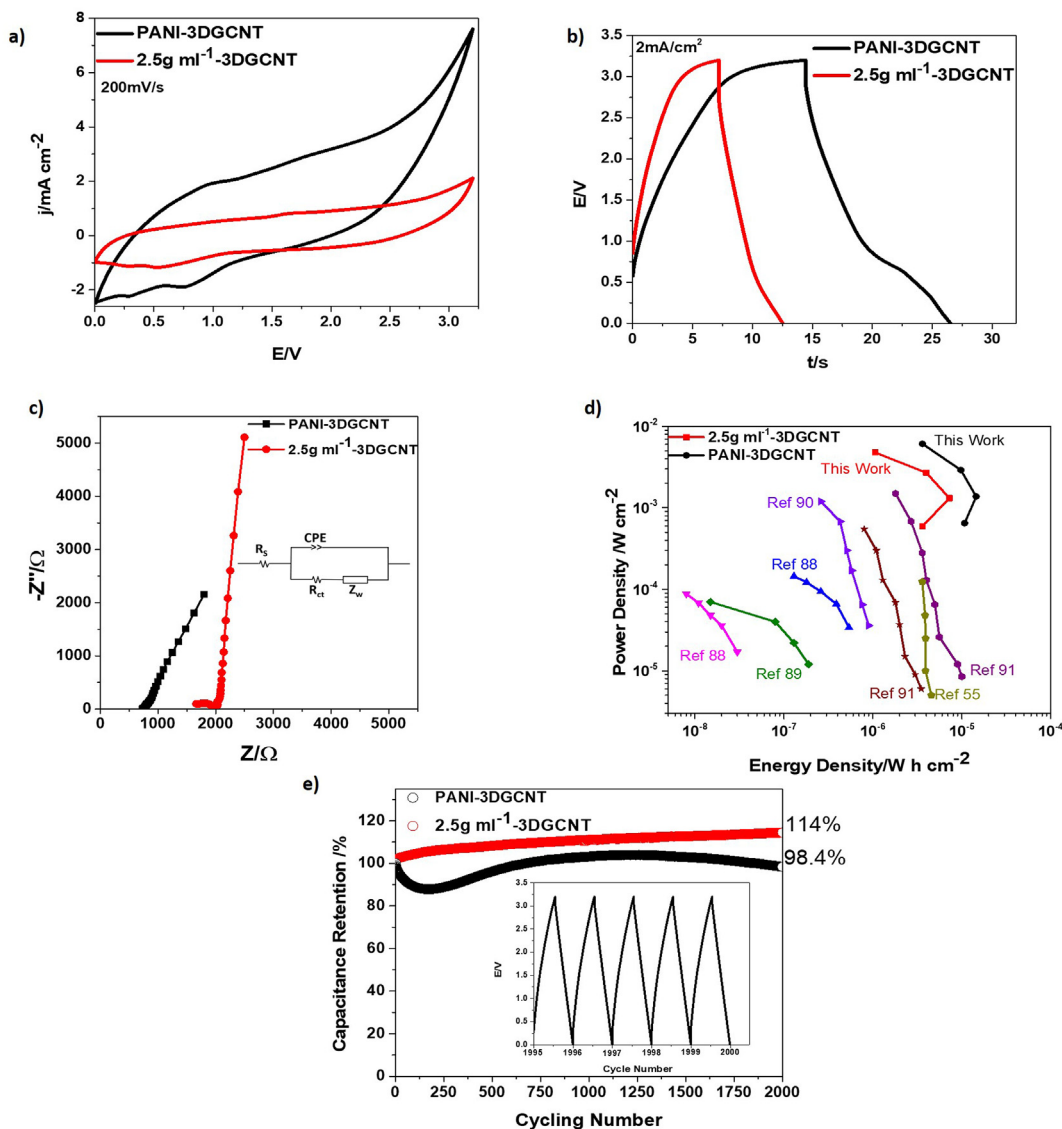


Fig. 9. a) Cyclic Voltammetry at 200mV/s for the 2.5gml⁻¹-3DGCNT and PANI-3DGCNT EMIMBF4 fiber devices; b) Charge-Discharge of 2.5gml⁻¹-3DGCNT fiber device at 2mA/cm², and of PANI-3DGCNT EMIMBF4 devices; c) Nyquist plots of 2.5gml⁻¹-3DGCNT and PANI-3DGCNT EMIMBF4 devices; d) Ragone Plot comparing EMIMBF4 devices with other similar fiber supercapacitors from the literature [55,88–91]; e) Cyclic Retention test for the 2.5gml⁻¹-3DGCNT and PANI-3DGCNT devices at 1 A/g (Inset: Charge-Discharge graphs from 1995 to 2000 cycles for the 2.5gml⁻¹-3DGCNT device).

recognize the pseudocapacitive effects of PANI, as well as the contribution of the ionic liquid (EMIMBF4) as an electrolyte.

In Fig. 9e is illustrated the long life and cyclic stability of the 2.5gml⁻¹-3DGCNT EMIMBF4 and PANI-3DGCNT supercapacitor devices by running a test over 2000 cycles at a current density of 1 A/g. It was observed that the 2.5gml⁻¹-3DGCNT device retained 114% of its initial capacitance over that time, whilst the PANI-3DGCNT device maintained 98.4% of its capacitance. The inset in the same figure displays the charge-discharge graph from 1995 to 2000 cycles for the 2.5gml⁻¹-3DGCNT supercapacitor. The increase in capacitance retention over 100% for the 2.5gml⁻¹-3DGCNT device can be ascribed to the activation of high porosity carbon within the fiber electrodes during the prolonged cycling, thus allowing a progressive wetting of the pores to take place. The porous structure of the 3DGCNT fiber shortened the diffusion length of the electrolyte ions and provided more active area for the electric double layer. The latter led to an enhancement of the capacitance after 2000 cycles [84–87]. The fabricated and tested electrodes in this work

revealed the ability of the described approach to produce devices with good cyclic stability and excellent capacitance retention.

The devices made from the PANI-3DGCNT were subjected to bending at different angles, as shown in Fig. 10a. The CV curves from that test were substantially similar and overlapped each other in most instances. In Fig. 10b, the fibers were bent at 180° a number of times and CV curves (200 mV/s) were taken. These curves maintained their shapes and size regardless of the number (cycle) of bends the device was subjected to. These experiments illustrated the flexibility and bendability of the fabricated devices.

In some instances of operation, high current or high operating voltages are expected from the energy storage devices. This can be achieved by connecting the devices in parallel or in series. CV curves of multiple PANI-3DGCNT devices connected in parallel and series are displayed in Fig. 10c and d. When the devices were connected in parallel (Fig. 10c) no change in the operating voltage was noticed, however, an increment in the current was observed. The devices were also wired in series, and expectedly, the operating

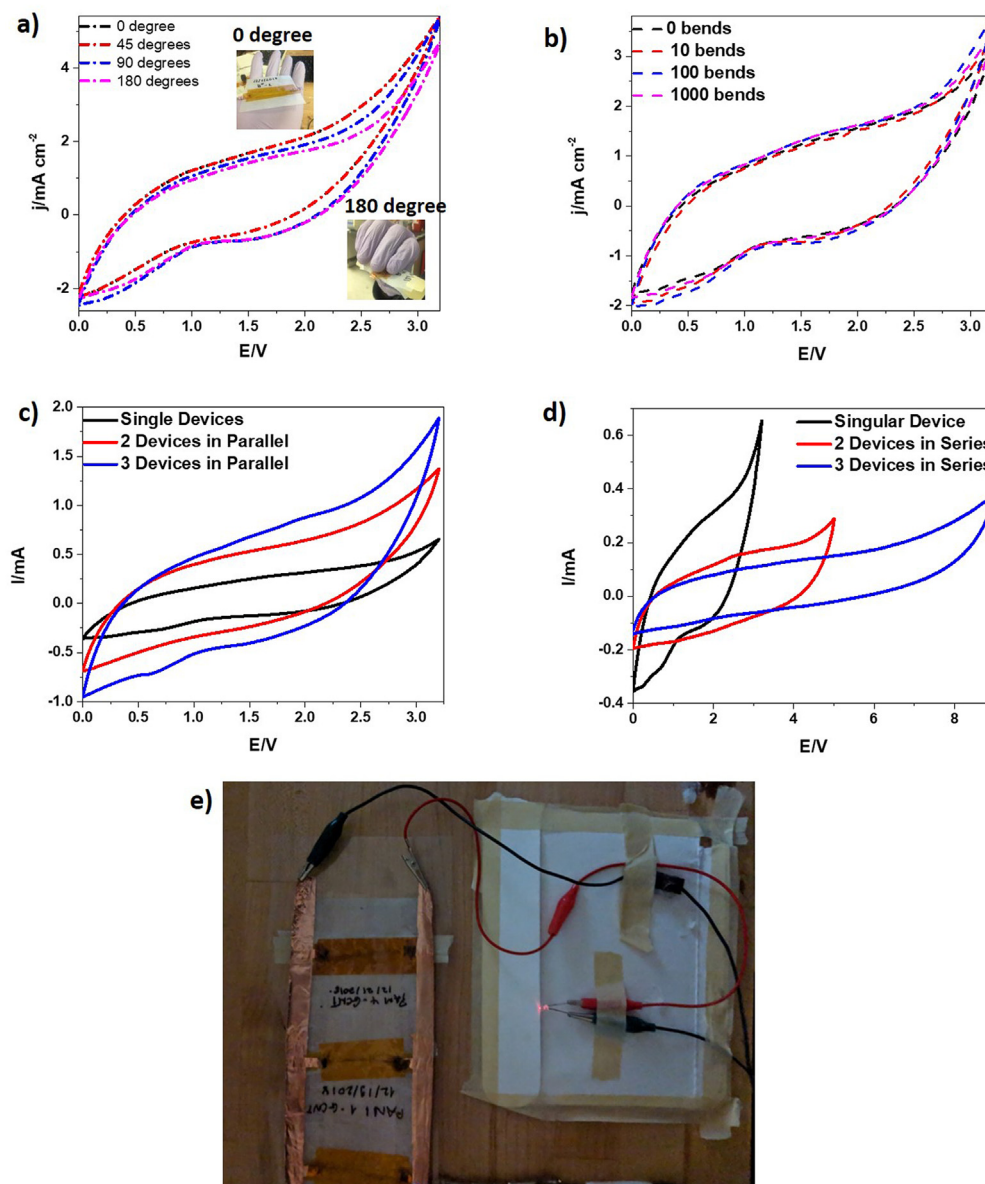


Fig. 10. a) CV curves of the PANI-3DGCNT device under different bending angles; b) CV curves of the PANI-3DGCNT device under bending; c) CV curves of multiple PANI-3DGCNT devices connected in parallel; d) CV curves of multiple PANI-3DGCNT devices connected in series; e) Digital photo of 3 PANI-3DGCNT devices powering a LED; [All CV curves have been obtained at a scanning rate 200mV/s.

voltage window of the combined supercapacitors was increased (Fig. 10d). Based on these tests, an experiment was set and the results of which are shown in Fig. 10e. There, three of the PANI-3DGCNT devices have been connected in parallel and working collectively powered a LED successfully.

Since we have not used any metal current collector for fabricating our devices, we obtained excellent gravimetric energy data,

as seen in Table 3. The Table gives a summarized comparison of the areal, volumetric, and gravimetric energy and power densities of the devices fabricated with the PANI-3DGCNT and 2.5gml⁻¹-3DGCNT fibers. PANI based devices produced energy and power densities larger than those from the 2.5gml⁻¹-3DGCNT. We believe that the demonstrated leveraging of the pseudocapacitive properties of PANI without suffering from significant drawbacks when

Table 3
Energy and power densities of PANI-3DGCNT and 2.5gml⁻¹-3DGCNT devices.

	2.5gml ⁻¹ -3DGCNT	PANI-3DGCNT	Charge Density
Areal Energy Density ($\mu\text{Wh}/\text{cm}^2$)	7.28	14.54	1 mA/cm ²
Areal Power Density (mW/cm^2)	1.31	1.37	1 mA/cm ²
Volumetric Energy Density (mWh/cm^3)	4.58	12.27	1 A/cm ³
Volumetric Power Density (W/cm^3)	1.34	1.39	1 A/cm ³
Gravimetric Energy Density (Wh/kg)	7.17	12.93	1 A/g
Gravimetric Power Density (W/kg)	1297.52	1350.25	1 A/g

using bulk PANI [92], was due to the active carbon nanostructured template (3DGCNT).

4. Conclusions

We have demonstrated a scalable process for synthesizing a hybrid graphene-CNT fiber electrode using CVD. The created and tested approach is continuous, simple and suitable for processing extended lengths of CNT fibers. The amount of graphene on the fiber was controlled by the viscosity of the slurry and the amount of Ni that was deposited on it. This processing allowed tuning some of the fiber's physical properties such as tensile strength and electrical conductivity. The fabricated fibers were characterized using tensile testing, a four-probe instrument, SERS, SEM, and electrochemical testing. The fibers were found to have excellent electrical conductivity and reasonable strength when compared to graphene fibers and other carbon-based hybrid fibers reported in the literature.

The fiber with the best electrochemical performance (2.5 g ml⁻¹-3DGCNT) was used to create supercapacitors free of any metal current collector or conductive additives. These devices showed an excellent rate performance with a high areal energy density and superior power density, compared to other similar supercapacitors. In addition, they demonstrated excellent cyclic stability attaining capacitance retention of about 114% after 2000 cycles.

Further, PANI nanorods have been successfully grown on the surface of the 3DGCNT fibers employing a chemical oxidative polymerization technique. The devices fabricated from these PANI-3DGCNT fibers revealed energy densities higher than those attained from the 3DGCNT fiber supercapacitors (14.54 $\mu\text{Wh}/\text{cm}^2$ vs. 3.96 $\mu\text{Wh}/\text{cm}^2$ at 1 mA/cm²), while maintaining similar power densities as the 3DGCNT fiber (1.37 mW/cm² vs. 1.52 mW/cm² at 1 mA/cm²). The PANI-3DGCNT device also demonstrated long life and cyclic stability by maintaining a high capacitance retention of 98.4% over 2000 charge-discharge cycles. The reported here 3DGCNT fibers behaved as good current collectors. There were flexible, binder-free, lightweight, free-standing, and performed very well without any metal collectors as part of their construction. All these qualities make them ideal electrodes for supercapacitor applications.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.electacta.2019.04.179>.

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