GRAPHENE BASED FIBER SHAPED SUPERCAPACITORS

Cakar O.[1], Gumrukcu S.[2], Top A.[3], Sezer E.[2], Ustamehmetoglu B.[2], Toomey A.[5] Cebeci H.[4], Ozden Yenigun E.[5]

[1]Department of Defence Technologies, Istanbul Technical University, Istanbul, Turkey;
[2]Department of Chemistry, Faculty of Science and Letters, Istanbul Technical University, Istanbul, Turkey;
[3]Department of Metallurgical and Materials Engineering, Faculty of Chemical and Metallurgical Engineering, Istanbul Technical University, Istanbul, Turkey.
[4]Department of Aeronautical Engineering, Faculty of Aeronautics and Astronautics, Istanbul Technical University, Istanbul, Turkey;
[5]School of Design, Textiles, Royal College of Art, London, United Kingdom;

Corresponding author: elif.ozden-yenigun@rca.ac.uk

ABSTRACT
Supercapacitors have been widely used in many applications from hybrid vehicles to smartphones due to their fast charge-discharge rate and high cycling stability. Nevertheless, traditional bulky supercapacitors have not responded well to the needs of smart wearables. Fiber shaped materials pushed the state of art by promising lightweight, flexible and robust wearable energy storage components. In this study, pristine GO fibers were spun wet-spinning method and then coated by pyrrole (Py). Promoted by $FeCl_3$, polymerization was completed and polypyrrole (PPy) coated GO fibers served as electrodes. This flexible PPy/GO fiber electrodes demonstrated a specific capacitance of 177.45 F/g.
Key Words: Graphene Oxide (GO), Supercapacitors, Cyclic Voltammetry (CV), Fiber Electrodes.

1. INTRODUCTION

Achieving flexibility while maintaining high-performance energy storage has driven the current research of supercapacitors from the solid-state-devices to more attractive platforms such as fabrics for wearable electronics [1]. At present, energy storage in smart textiles has remained as a challenge to power wearable systems [2]. Compared to conventional batteries and solid-state-devices, elastic fiber shaped supercapacitors with fast charge-discharge rate and high cycling stability is essential to be capable of full integration into cloth [3][4][5]. Additionally, these novel energy storage materials need to be durable, non-toxic, scalable and cost-effective ensuring user-friendliness and the seamless integration of technology into the fabric.

Demand for high performance, safe and cost-effective supercapacitor electrodes can be fulfilled with carbon-based materials. Several studies were performed to employ varied existing forms of carbon as powders, fibers, felts, composites, mats, monoliths, and foils [5]. Although porous carbon has a high specific surface area, the low electrical conductivity limits its application for supercapacitors. Recently, fiber-shaped supercapacitors from carbon fibers (CFs) [6] conducting polymer and/or metal oxides doped carbon nanotubes (CNTs) [7], pristine CNTs and reduced graphene oxide (rGO) fibers and their composites blended with conducting polymers [8] which exhibited excellent stability but comparatively low volumetric energy density to traditional and massive supercapacitors [9], have been studied. Among these, graphene oxide (GO) fibers demonstrated high packing density and large-ion contact area, chemical stability and higher electrical conductivity for an efficient energy density without sacrificing flexibility.

To date, it is still a significant challenge to achieve elastic fiber shaped supercapacitors with high pseudocapacitance along with enhanced energy and power density. Boosting the overall electrochemical performance of graphene-based fibers, a reinforcing strategy through doping these fibers with conducting polymers such as polypyrrole (PPy) [10], polythiophene (PTh) [11] and polyaniline (PANI) [12] was studied. Decorating surface by either by coating or doping with functional materials provides many advantages for electrochemical studies [13]. Hence,

PPy has been found promising as electrode material within its ease of synthesis, stability and suitable oxidation/reduction mechanism [14].
This study focused on assessing the use of pristine and PPy coated GO fibers for supercapacitor electrodes. A custom-built wet spinning line produced these meter-scale continuous GO fibers. This easy, simple and green method allowed us to spin micron-scale flexible GO fibers with tunable mechanical and electrical properties. Different processing conditions of feeding rate at 0.2, 0.3 and 0.7 mL/min optimized through production was adjusted by monitoring changes in mechanical properties. PPy/GO fibers were produced by the dip-coating of GO fibers with PPy to enhance both electrical conductivity and capacitive behavior. Hence, diameters of fibers were quantified by stereo microscopes (Carl Zeiss Stemi 2000-C), mechanical properties were measured by Universal Testing Machine (UTM) (Shimadzu AGX-Plus), and surface morphology was observed by FE-SEM (A FEI-Qanta FEG250, USA). The results suggested that GO fibers with a diameter of 137.57 ± 4.63 μm later used as electrode exhibited ultimate strain (%) of 11.63 ± 1.19. The cyclic voltammetry (CV) measurements revealed that PPy coating promoted better electrochemical properties where a specific capacitance of 177.45 F/g of PPy/GO fibers was achieved.

2. MATERIALS AND METHOD

2.1 Materials

GO dispersion (12 mg/mL, aqueous) was supplied from Graphitene (UK) with monolayer graphene sheets in 0.5-5 μm lateral size. Calcium chloride ($CaCl_2$) (anhydrous, powder, ≥97%) were purchased from Merck. A custom-built GO fiber spinning line was employed to draw GO fibers. Pyrrole (Py), acetonitrile (ACN) and iron (III) chloride ($FeCl_3$) (reagent grade, 97%) were employed for the coating of GO fibers, and ethanol used in coagulation bath and methanol in washing bath, all were purchased from Sigma-Aldrich. Potassium hydroxide (KOH) were purchased from Merck for electrochemical measurements. All of these chemicals were analytical grade and used without further purification.

2.2 Wet-spinning of GO Fibers and Coating of GO Fibers with PPy

Meter-long continuous GO fibers were produced by custom-built GO fiber spinning line depicted in Figure 1.a. The same protocol proposed by our research group was used to spin GO fibers [15]. The designed spinning line consisted of a mixer/piston system to mix and inject GO solution through a spinneret into a coagulation bath. In this study, aqueous GO liquid crystals (GOLCs) were injected through a spinneret into the coagulation bath at a feeding rate of 0.2, 0.3 and 0.7 mL min-1. With the aid of the molecular orientation and alignment of GOLCs, GO fibers were solidified in a rotating coagulation bath at 10 rpm as shown in Figure 1b. $CaCl_2$ was used for coagulation bath with 5 wt.% in 1:3 (v/v) ethanol:DI water solutions. The process was then followed by methanol washing to remove the residual coagulation chemicals. Fibers were then transferred and collected by a winding drum at a speed rate of 6 rpm. The custom-built system was designed where main factors affecting the overall fiber properties such as flow rate, take-up speed, and draw ratio can be precisely controlled. GO fibers in the coagulation bath were placed onto collecting drums manually and then were spun by enabling stretch by winding. A real photo image of GO fibers, collected and dried for 24 hours at room temperature, is given in Figure 1c and homogenous and uniform diameter along the GO fibers can be seen in microscopy images (Figure 1c).

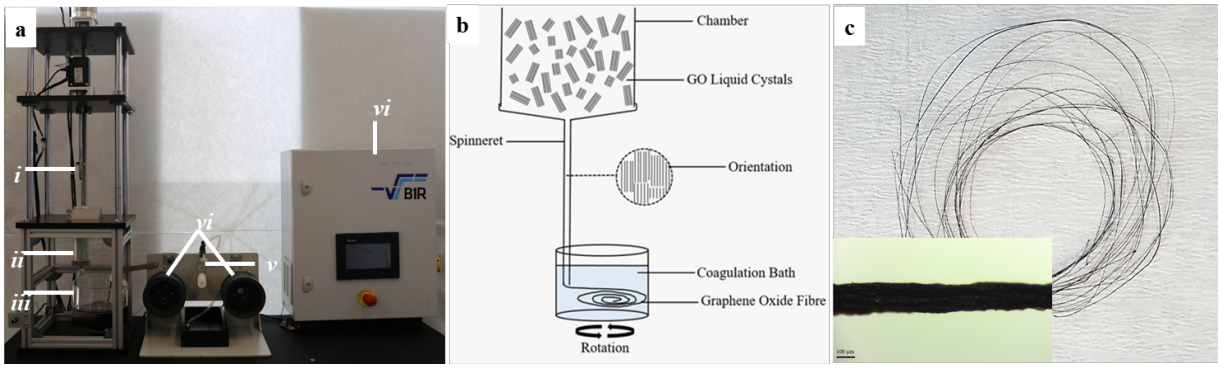

Figure 1. Custom-built GO wet spinning line at ITU ARC. a. (*i*) mixer and piston (*ii*) reservoir (*iii*) coagulation bath (*iv*) collecting drums (*v*) methanol shower (*vi*) control panel to adjust process parameters. b. Schematic view of drawing GO fibers and alignment of GO liquid crystals. c. True camera image and optical microscopy image of pristine GO fiber.

Coating of GO Fibers with PPy: These as-spun GO fibers were coated by dipping to produce flexible and conductive fiber based supercapacitors. This procedure began with dipping GO fiber into a reactant Py monomer solution for 15 seconds. Then, these fibers (Py/GO) were immersed into 0.01 M $FeCl_3$/ACN solution and dried at room temperature. Brownish GO fibers became black when the formation PPy (PPy/GO) was successfully completed. These PPy/GO fibers were later used as electrodes.

2.3 Mechanical Properties of the Fiber Electrodes

The mechanical performance of pristine GO fibers which were extruded at a feeding rate of 0.2, 0.3 and 0.7 mL min^{-1}were evaluated by a single fiber tensile test by UTM, equipped with a 1kN load cell (1mN sensitivity). At least 10 test samples for each fiber were prepared with 25 mm of the gauge length. Test head speed was kept constant at 0.5 mm min^{-1} during the test as defined at ASTM D3379-75 [16]. Each specimen was attached to a paper frame as depicted in Figure 2a-2b and gripped as displayed in Figure 2c. Then Py/GO and PPy/GO fiber electrodes were evaluated for their mechanical properties under the same conditions.

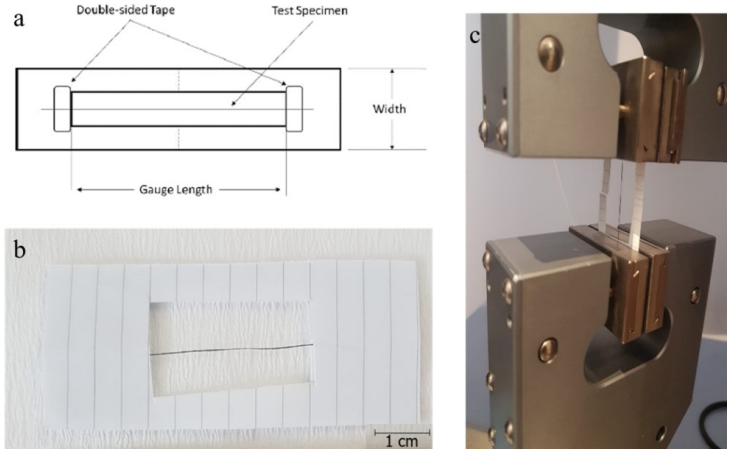

Figure 2. (a) Schematic of the test sample (b) Single fiber mechanical test sample (c) Implementation of single GO fiber for tensile testing.

2.4 Electrochemical Measurements

Electrochemical performances were investigated by CV, where pristine GO, Py/GO and PPy/GO electrodes as the working, Ag wire as a reference and Pt wire as counter electrodes were used. All capacitance measurements were performed in 6M KOH aqueous electrolyte in

a 3-electrode cell set-up, implemented in a Parstat 2263 electrochemical workstation. CV curves were tested at different scan rates with the potential range from 5 to 200 mVs^{-1}.
Specific capacitance was calculated using Equation-1 as depicted below;

$$\boldsymbol{C = \int_{E1}^{E2} iEdE \,/\, 2\,(E2 - E1)\,mv} \qquad \text{(Equation-1)}$$

where *C* is the specific capacitance of the individual sample. E_1, E_2 are the cut-off potentials in CV. *i(E)* is the instantaneous current. $\int_{E1}^{E2} iE\,dE$ is the total voltammetric charge obtained by the integration of positive and negative sweep in CV. $(E_2 - E_1)$ defined as the potential window width. *m* is the mass of individual samples, calculated as the mass difference of the working electrode before and after coating. *v* is the potential scan rate.

3. RESULTS AND DISCUSSION

SEM images suggested well aligned and interconnected GO sheets along the fiber axis were revealing a certain degree of surface roughness as in (Figure 3a). Besides, it is very well known that their lateral size and degree of alignment played a significant role in the fiber production which has an effect on continuous and large scale production and as well as mechanical and electrical properties of GO fibers [17][18]. The GO fibers can be easily overhand knotted as can be seen in Figure 3b due to their superior flexibility. SEM images of the Py and PPy coated GO fibers in **Error! Reference source not found.**c-3d demonstrated a successful coating process. More importantly, due to increased surface roughness and creased surface topology, as seen in (**Error! Reference source not found.**c-3d), the surface area of fiber-shaped capacitors were enhanced. After the coating of Py and PPy, the diameter of Py/GO fibers and PPy/GO fibers was increased and recorded as 144.7 and 177.16 µm, respectively. This increase attributed to new layer deposition onto the surface.

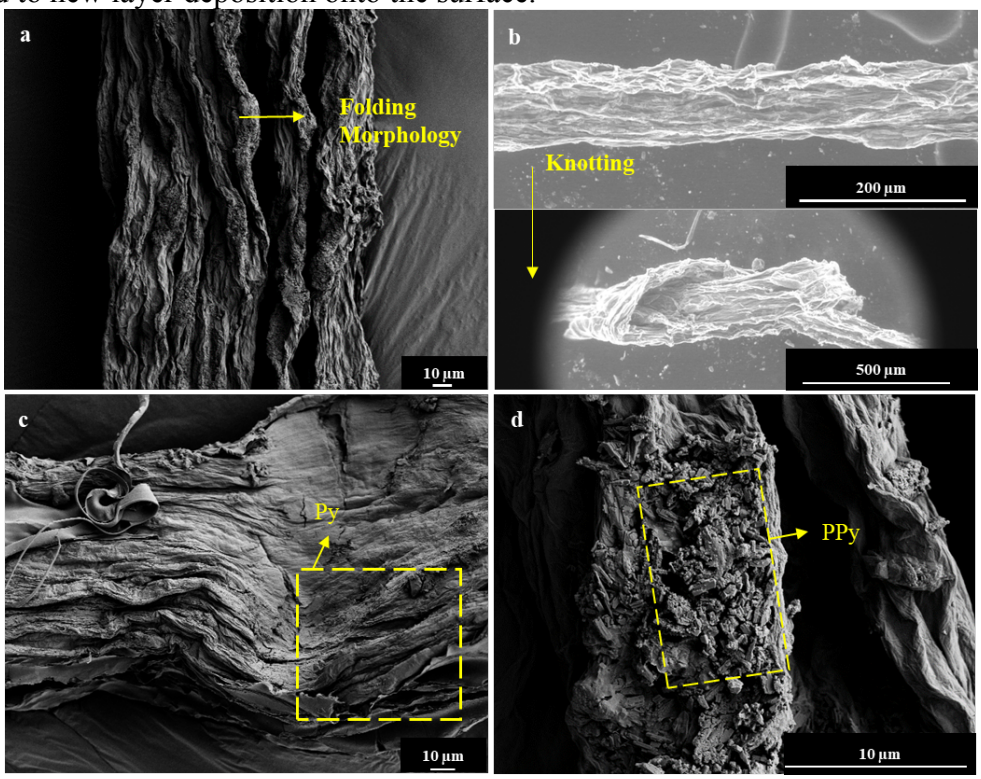

Figure 3. SEM images of the (a) knotting of pristine GO fiber (b) pristine GO fibers with folding morphology, (c) Py coated GO fibers, (d) PPy coated GO fibers.

Mechanical tests pointed out that the ultimate strain % of GO fibers produced at 0.2, 0.3 and 0.7 mL min^{-1} were found as 4.85 ± 1.69, 6.76 ± 1.93 and 11.63 ± 1.19, respectively. Hence, the superior flexibility of GO fibers spun at 0.7 mL min^{-1} was drastically higher than reported data

in literature as of 6.8-10.1 % [19]. However, PPy coating caused a significant decrease in ultimate strain% by 34.18% as depicted in Table 1. PPy has been known as low cost, easily synthesizable and relatively high conductive but its forms are quite often mechanically weak and brittle. This PPy coating resulted in the reduction of elongation of GO fibers. Nevertheless, suppressed elongation values found still higher than the reference studies [19]. In a wearable context, when integration of fiber electrodes into cloth through weaving and knitting becomes the priority, strain ability would be critical as fiber strength.

Table 1. Single fiber tensile test results.

Sample	Ultimate Strain (%)	Specific Stress mN/tex	Diameter (µm)
Pristine GO Fiber	11.63 ± 1.19	2.95 ± 0.23	137.57 ± 4.63
Py/GO Fiber	6.31 ± 0.76	4.61 ± 0.26	144.7 ± 2
PPy/GO Fiber	7.69 ± 1.34	7.41 ± 0.37	177.16 ± 2.18

The theoretical specific capacitance of single-layer graphene if the entire surface area is fully responsive was found as 550 F g^{-1} [20]. In several studies, it is clearly demonstrated that this value was lower than it was anticipated due to strong π-π interaction and van der Walls attractions where graphene tended to agglomerate and actual specific surface area and conductivity decreased.

The specific capacitance is a crucial indicator to address the performance of electrodes. When pristine GO fibers were used as working electrodes in 6 M KOH in order to reveal their potential as both the active material and the current collector, they exhibited slightly lower capacitive performance. While Py and PPy coated GO fiber electrodes demonstrated a different profile as seen in Figure 4. The cycle area of each CV curve in PPy/GO was more abundant than in pristine GO and Py/GO fiber electrodes. Among these fiber electrodes, PPy/GO promised the highest specific capacitance of 177.45 F g^{-1}, whereas pristine GO and Py/GO fiber had 79.62 F g^{-1} and 136.89 F g^{-1} at 5 m V s^{-1} scan rate, respectively. Overall, the results suggested that specific capacitance value dramatically increased by PPy coating onto GO fiber electrodes, and revealed higher performance than the reference study [21]. The selection of 6 M KOH was also intentionally due to its highly ionic conductivity, small size and the high mobility of OH^- anions in aqueous solutions. Thus, high concentration was preferred to increase the ion diffusivity and the ionic conductivity of the electrolyte.

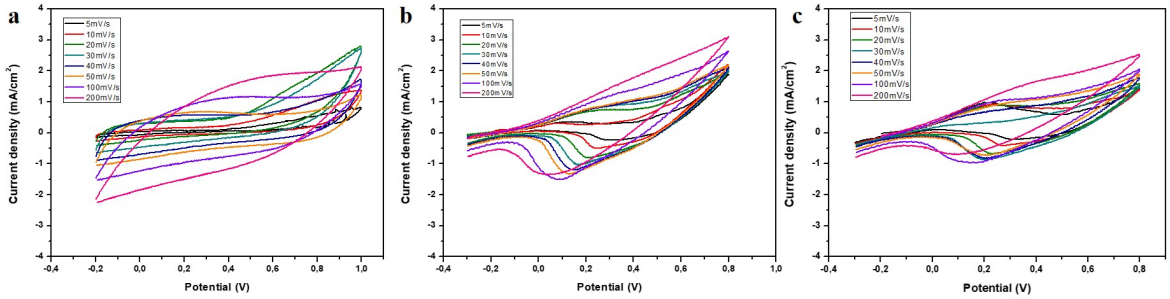

Figure 4. CV curves at varying potential scan rates ranging from 5 to 200 mV s^{-1} (a) Pristine GO fiber, (b) Py/GO fiber, (c) PPy/GO fiber electrodes.

4. CONCLUSION

This study highlighted the production of graphene-based fiber supercapacitors which are flexible and robust enough for further textile processes including weaving and knitting. The experimental procedure began with the spinning of GO fibers by controlling the liquid crystal phase of GO suspensions. These continuous fibers were further modified by using conductive Py and PPy as one of the most attractive electrode materials for supercapacitors due to its high doping-dedoping rate. Tensile tests indicated a high level of stainability up to 12% which eased

post-processes such as weaving for the integration of these supercapacitors into cloth. GO fibers coated by PPy dramatically improved cycle stability and specific capacitance compared to pristine GO fibers.

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