

Capacitance of Flexible Polymer/Graphene Microstructures with High Mechanical Strength

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ABSTRACT

Carbon-modified fibrous structures with high biocompatibility have attracted much attention due to their low cost, sustainability, abundance, and excellent electrical properties. However, some carbon-based materials possess low specific capacitance and electrochemical performance, which pose significant challenges in developing electronic micro-devices. Here, we report a microfluidic-based technique of manufacturing alginate hollow microfibers incorporated by water dispersed modified graphene (BSA-graphene). These architectures successfully exhibited enhanced conductivity about 20 times higher than alginate hollow microfibers without any significant change in the inner-dimension of the hollow region ($220.0 \pm 10.0 \mu\text{m}$) compared to pure alginate hollow microfibers. In the presence of graphene, higher specific surface permeability, active ion adsorption sites, and shorter pathways were created. These continuous ion transport networks resulted in improved electrochemical performance. The desired electrochemical properties of the microfibers make alginate/graphene hollow fibers an excellent choice for further use in the development of flexible capacitors with the potential to be used in smart health electronics.

Keywords: *Alginate/Graphene; Microfibers; Conductivity; Ion Transport; Capacitor.*

I. INTRODUCTION

In developing supercapacitors, one substantial key is the design of active nano and macro structures with high electrochemical performance. In this context, polymer fibers with small volume, lightweight, and high power density have attracted considerable attention in various electronic fields such as static charge dissipation, fiber-based portable, and wearable electronics storage ¹⁻⁷, sensors ⁸⁻¹³, actuators ¹⁴, and electromagnetic interference shielding ¹⁵. Moreover, to enhance the electrical conductivity and charge storage potential of these fibers, various studies were conducted introducing metal filaments ¹⁶⁻²⁰, intrinsically conductive polymers ²¹⁻²³, carbon black ²⁴, graphite and graphene ²⁵, carbon nanotubes, and carbon nanofiber ²⁶⁻²⁹ as conductive modifiers ^{30, 31}.

Graphene with a maximum number of covalently-bonded carbon atoms per mass unit could induce exceptional electrochemical behavior and more superficial porosity with shorter transport distances to these host polymer systems. Numerous studies have been published on the successful modification of polymer fibers by graphene to create conductive carbon nanoparticles/polymer composites with high biocompatibility and specific conductivity in many aspects of biomedical applications ³²⁻³⁵. In this respect, a few fabrication techniques for the preparation of these conductive composite fibers such as microfluidics ^{13, 36-40}, electrospinning ⁴¹⁻⁴³, wet-spinning ^{8, 12, 44, 45}, melt-spinning ⁴⁶⁻⁴⁸, dry-film scrolling, ⁴⁵ centrifugal spin ⁴⁹, and tube membrane ultrafiltration ⁵⁰ have been widely reported. Compared to other techniques, microfluidic is a promising pathway with a high potential for continuous fabrication of fibers at a large scale due to its high facility and cost-effectiveness ⁵¹⁻⁵⁸. Hence, the microfluidic technique has played impressive roles in developing single or multi-compartmental scaffolds in tissue engineering ⁵⁹⁻⁶³.

Moreover, the microfluidic method developed conductive hollow microfibers with a significant surface to the volume value, considered high-performance supercapacitors for applications ranging from energy to biomedical engineering ^{38, 64}. Since the electrochemical behavior of such fiber supercapacitors demand further investigation, a novel five-channel microfluidic device was employed in this report to study the continuous fabrication of conductive alginate hollow microfibers through a mild gelation procedure in the

presence of Ca^{2+} . Alginate was chosen as a substrate because it is a popular natural biofunctional hydrogel with adequate mechanical properties and a homogenous structure⁶⁵⁻⁶⁹. We have previously shown that microfluidic spun microfibers have higher tensile stress at break and Young's modulus⁴⁰. We have also demonstrated higher mechanical strength in our microfibers because the shear force exerted on the prepolymer solution aligns the polymer chain in the flow direction.

We know of no previous reports regarding the employment of water dispersed bovine serum albumin (BSA)-graphene as an electrically conductive modifier for hollow alginate microfiber produced by a five-channel microfluidic chip. Moreover, this microfluidic approach can manufacture variable dimensions of hollow microvessels by merely altering the flow rate ratio (FRR) of the inlet solutions. Additionally, this approach does not require any post-processing technique to fabricate hollow microfibers and produces long microfibers with high throughput. We aim to evaluate the manufactured hollow alginate/graphene compositions and FRR between the core and sheath fluids on the hollow microfibers' morphology and electrical conductivity properties. The obtained results confirm the potentials of hollow alginate/graphene microfibers as flexible and biocompatible structures for achieving capacitance and conductivity in chip implants and smart electronic health gadgets.

II. EXPERIMENTAL

A. Materials

3.5% sodium alginate solution (Product Number A18565) was prepared, which was bought from Alfa Aesar, Ward Hill, MA. Poly (ethylene glycol) (PEG) (Mn = 400, Aldrich Chemistry, St. Louis, MO) containing 0.04% $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ (Fisher Chemical, Waltham, MA) was used as the sheath solution. A container with an aqueous solution of 15% CaCl_2 was chosen to collect fibers. For the preparation of graphene dispersed water, graphite powder (Synthetic graphite powder <20 μm) and bovine serum albumin BSA (A7906) were purchased from Aldrich Chemistry, St. Louis, MO. The AlTiN-coated end mill cutters and drill bits were purchased from Harvey tools and Grainger. Ultra-pure water (18.2 $\text{M}\Omega \cdot \text{cm}$) was obtained

from a Thermo Fisher Scientific water system (Waltham, MA). All chemicals were of AR grades and used without further purification.

B. Instruments

The electrical behavior of the hollow microfibers was determined by electrochemical impedance spectroscopy (EIS), cyclic voltammetry (CV), and galvanostatic charge/discharge (GCD) and using a potentiostat system (Versa STAT 4, Princeton Applied Research, Princeton, USA). A JCM-6000 NeoScope benchtop scanning electron microscope (SEM) (Nisshin EM. CO., LTD, Tokyo, Japan) was used to study the morphology of the manufactured hollow microfibers. Differential scanning calorimetry analysis (DSC) of the samples was carried out using the Mettler Toledo DSC instrument (Mettler Toledo 823 DSC, Switzerland), under a heating rate of 10 °C/min, and at atmospheric pressure. The surface functional groups on the prepared samples were verified by a Fourier transform infrared spectrometer (FTIR, PerkinElmer, Frontier, USA) over 3500–750 cm^{-1} . Three Lucca Technologies GenieTouch™ dual-channel syringe pumps were used to drive two 20 mL syringes.

C. Preparation of BSA-Graphene Samples through Ball Milling Process

The BSA-graphene samples were synthesized based on our previous method reported⁷⁰. Briefly, this Few-Layer graphene was fabricated through the exfoliation of graphite crystallites. An aqueous mixture consisting of graphite (20.00 mg mL^{-1}) and BSA (2.00 mg mL^{-1}) was prepared in plastic containers containing steel balls with diameters 1/2", and 11/32", respectively to induce shear stress at 300 rpm rotational speed. The overall ratio of the balls was kept constant at $500 \pm 10 \text{ m}^2/\text{m}^3$ in order to maintain the surface to volume ratio. The plastic containers were sealed and placed inside the metal containers, and the whole assembly was agitated for 90 h to initiate the exfoliation process.

D. Fabrication of Microfluidic Devices

As previously reported by our group ⁷¹, a five-channel microfluidic device was used to fabricate hollow microfibers. The channel was developed from 6.0 mm thickness Poly (Methyl Methacrylate) (PMMA, Grainger, IL, US). A computerized numerical control (CNC) mini-mill (Minitex Machinery Corporation, Norcross, GA) was used to mill the core channels and the two independent sets of chevrons with a dimension of 1.00 mm × 0.75 mm (width × height) and 0.375 mm × 0.25 mm (width × height), respectively. Two PMMA chips were milled separately and eventually aligned and bonded together to obtain a microfluidic device.

E. Fabrication of Hollow Alginate/Graphene Microfibers

FIG. 1 shows the diagram of the microfluidic pathway developed in the current study. The syringe containing the core solution was connected to the center channel inlet, and the sample and sheath solutions were respectively pumped into the middle and last twin inlet channels of a five-channel microfluidic device by individual syringes. These solutions flowed through their respective inlets and syringe pumps at constant fluid flow rates of 200: 450: 230 $\mu\text{L}/\text{min}$ (sheath: core: sample). Solid or hollow microfibers can be formed from the alginate solution during a cross-linkage procedure in the presence of Ca^{2+} . The core and sheath solutions remained in the water bath after dissolving into the CaCl_2 solution. The produced hollow microfibers were collected using a set of tweezers and safely mounted onto paper frames. These hollow microfibers were then dried overnight at room temperature.

III. Results and Discussion

We employed the five-channel microfluidic device equipped with two chevron regions to continuously manufacture these hollow alginate microfibers, as shown in FIG 1. The design contains a microchannel with three inlet channels converging onto the core channel owning two sets of four chevron-shaped grooves

extending vertically and twin three inlet channels located on either side. Hollow alginate composite microfibers were fabricated based on the rapid exchange and diffusion phenomena inside the microfluidic channel with a specific surface area and under a laminar flow regime. Next, the sheath fluid (PEG) enters the microfluidic channel from the last set of inlets to separate the polymer fluid from the walls and hydrodynamically focus the hollow fiber solution.

The sizes of hollow microfibers were directly influenced by the flow rate ratio (FRR) between the solutions, which caused a hydrodynamic focusing procedure along the microchannel sidewalls. Hence, detailed hollow dimensions of prepared microfibers at different FRR were investigated as the most crucial parameter (FIG. 2.)

The hollow size decreased from 260.0 μm to 220.0 μm by increasing the FRR from 0.33 to 0.44 due to the enhancement of hydrodynamic focusing by increased FRR. At a lower flow rate ratio, the applied hydrodynamic focusing on polymer fluid has decreased. As a result, the width of hollow fibers has increased in the lateral direction. The size of the hollow fibers was observed to increase in size from FRR 0.44 to 0.5. This increase in the size of the hollow fibers can be attributed to the increase of the sheath flow rate above a threshold value. After the sheath flow rate exceeds a certain flow rate, the amount of fluid entering the set of chevrons increases resulting in the higher advection of the polymer solution eventually furnishing microfibers with increased size. At FRR of 200.0: 450.0: 230.0 $\mu\text{L}/\text{min}$ (sheath: core: sample) point, the maximum hydrodynamic focusing was applied on alginate fluid for construction of hollow alginate microfibers, which was chosen as the optimum FRR point for subsequent steps. After adding BSA-graphene to the alginate solution, the viscosity of the obtained polymer fluid increased, resulting in a weakened hydrodynamic focusing from the core flow. Therefore, the FRR for alginate/graphene had been insignificantly shifted to smaller values to compensate for this weakness.

SEM was used to analyze the morphology of the hollow microfibers and determine the sizes of these hollow microfibers (FIG. 3). As shown in FIG. 3, the average inner-dimension was about $220.0 \pm 10.0 \mu\text{m}$ for

hollow alginate and hollow alginate/graphene microfibers, and no noticeable changes were observed in sizes of hollow microfibers after graphene was introduced to polymer solutions. In addition, the incorporation of graphene into alginate did not significantly change the morphology of the fibers. Due to the different degrees of contraction between alginates and alginate/graphene particles during the gelation procedure, both samples showed porosity on their inner and outer surface. Detailed chemical characterizations of the synthesized BSA-graphene were described in our previous work ⁷⁰.

Differential scanning calorimetry (DSC) was used to determine the thermal behavior of the hollow alginate and alginate/graphene microfibers focused by PEG solution. The thermal results obtained under a heating flow rate of 10 °C/min are presented in FIG. 4. These DSC thermograms show an endothermic peak at ~85 °C related to the evaporation of water molecules and the oxidative degradation of alginate polymers and their calcium–carboxylate bonds as an exothermic peak at ~251 °C ⁷². In addition, these DSC thermograms displayed sharp melting endothermic peaks at ~65 °C related to PEG as an employed capping layer. Based on the DSC results, the oxidative degradation of alginate polymers occurred at ~251 °C, and by adding graphene, this peak shifted to higher values that shows graphene improved the thermal stability of the alginate fibers. For the hollow alginate/graphene microfibers, a distinct endothermic event was observed at ~350 °C that is related to oxygen elimination reactions of carbon atoms fundable in employed graphene structure, which could successfully confirm the presence of graphene inside the preparation of hollow microfibers without any significant impact on the crystal structure of alginate hollow microfibers. FIG. S1 shows the XRD pattern of graphene obtained from Hummers' method. Graphene shows two sharp peaks at $2\theta = 21.5$ and $2\theta = 35.47$, attributed to the interlayer distances of 4.1 and 2.5 °A, respectively. The peaks come from the functional groups on the graphene layers. X-ray diffraction (XRD) spectrum were recorded using Cu K α radiation between 5 and 40 (2θ). Our previous work reported the mechanical property of alginate fibers under different FRRs and CaCl₂ concentrations ⁷³. We showed that Young's modulus for alginate fibers was enhanced to 75 MPa. The tensile stress obtained for alginate fibers created under various FRR was enhanced ten times (~15 MPa) by increasing the CaCl₂ concentration from 0 % to 5 % ⁷³.

The Fourier transform infrared spectroscopy (FTIR) spectroscopy was used to characterize the surface factor groups that appeared during the formation of the hollow alginate microfiber. FIG. 5 compares the FTIR spectra of alginate hollow microfibers before and after the addition of graphene.

It is evident that the characteristic broad absorption band around 3350 cm^{-1} corresponding to the O–H stretching, the C–H stretching bond groups of O–C–H group functions are apparent in the range from 2800 to 2900 cm^{-1} , and the –C–O– stretching are apparent from 1000 to 1200 cm^{-1} . These results provide clear evidence for covering these hollow microstructures by PEG. The observed bands at 1627 cm^{-1} and 1465 cm^{-1} are attributed to asymmetric and symmetric stretching vibrations of the linkage between Ca and carboxylate functional group of alginate, respectively.

In addition, the electrical conductivity of the alginate and alginate/graphene hollow microfibers was investigated through the cyclic voltammetry (CV) method at the potential range -1.0 to $+1.0\text{ V}$ as a dependent factor to graphene amount (FIG. 6 (a)). In this order, two fibers (length $\approx 5\text{ cm}$) laid parallel on a polyethylene terephthalate (PET) substrate and were 5 mm apart. The endpoints of these hollow fibers were adhered to the carbon tape stuck on the PET substrate, and silver paste was applied to have a smooth connection. The preparation of the hollow alginate/graphene microfibers onto a coated thin layer of $\text{H}_3\text{PO}_4/\text{PVA}$ gel electrolyte is as follows:

$1.0\text{ gr H}_3\text{PO}_4$ and 1.0 gr PVA were mixed with 10.0 mL ultrapure water and vigorously stirred at $80\text{ }^\circ\text{C}$ for 3 hours to obtain a homogeneous and transparent gel. The versatile solid-state fiber-shaped electrodes were prepared by filling the $\text{H}_3\text{PO}_4/\text{PVA}$ gel in the gap between the fibers, overlapped, and then dried at room temperature. FIG. 6 (a) shows the representative CV results for the manufactured alginate hollow microfibers containing the various percentage of graphene in the potential range from -1.0 to $+1.0\text{ V}$ (vs. Ag/AgCl) with a scan rate of $10.0\text{ mV}\cdot\text{s}^{-1}$ at $21\text{ }^\circ\text{C}$.

As seen, these peak currents in the CV curves related to hollow alginate/graphene microfibers improved by almost a range factor 10-25, and the voltage window increased, from 0.5 V to 1.0 V at a 10.0 mV s⁻¹ scan rate, which could successfully confirm the induction of electrical conductivity to hollow alginate microfibers as a result of incorporating graphene.

Compared to pure alginate samples, the broader peak area and a nearly rectangular behavior with high stability were exhibited by hollow alginate/graphene microfibers, and CV results could be considered the effects of electric double-layer series. The hollow graphene composite alginate microfibers introduced an acceptable energy-storage capability and effective ion transport. Unexpectedly, increasing the graphene amounts by more than 0.25% did not provide any more conductivity enhancement for the development of hollow alginate/graphene microfibers due to the loss of porosity manner of these structures.

For further confirmation of the charge transmission and ion transport enhancement obtained from the developed alginate structures, the percentage of 0.25% graphene as an optimum amount of a conductive modifier, the CV characterization was continued under various the scanning rate from 10.0 to 2000.0 mV s⁻¹. As seen in FIG. 6 (b), the CV plots became more eye-shaped by increasing the scan rate up to 2000.0 mV s⁻¹ due to limitations for ion mobility in the PVA/H₂SO₄ gel electrolyte voltage variation at a high scan rate. In addition, these obtained results clearly showed the stability related to the electric double-layer capacitance associated with hollow microfibers over the whole voltage range.

Furthermore, the EIS technique investigated the dielectric, ion-transport behaviors, and ion kinetics manners of the prepared microfluidic alginate hollow microfibers before and after adding graphene to this structure. As shown in FIG. 7 (a), the obtained Nyquist plots comprised semicircular curved reigns obtained in two regions: the high and medium frequency region referred to the total ohmic resistance or the charge-transfer reaction resistance. Moreover, the second trailed straight lines curves that appeared in the low-frequency region could reflect the diffusion process inside these structures. These straight lines obtained in the low-frequency range for hollow alginate/graphene microfibers samples show higher rates (slopes) than alginate samples due to the higher availability of active electro sites inside hollow alginate/graphene microfibers.

As a result of the increased porosity and ions transporting pathways for the hollow alginate/graphene microfibers, greater ion diffusion manner to hollow alginate microfiber samples obtained by the added graphene as a conductive modifier ⁷⁴. The hollow alginate/graphene microfibers samples successfully exhibited less $|Z''|$ in the high-frequency range with their enhanced conductivity compared to hollow alginate microfiber. However, the upward trend was not achieved for hollow alginate/graphene microfiber by increasing the graphene amount from 0.5 % to 1.0 % because of losing the obtained porosity manner at these percentages.

The specific capacitance behavior of prepared hollow microfibers was investigated as the most critical feature to confirm their supercapacitor behavior by galvanostatic charge/discharge technique under current densities (j) of 0.5 A/g. The results obtained from this study are shown in FIG. 7 (b).

The hollow alginate microfibers samples exhibited an enhancement in charge/discharge at 0.5 A/g with symmetry and triangular behavior. By adding the graphene percentage from 0 - 0.5%, hollow alginate/graphene microfibers could express more benefit in charge/discharge procedures with a large peak current, long discharging time, and no apparent ohmic loss (IR drop) at the low current densities compared to hollow alginate fibers. A lack of loss is because of sufficient electrical double-layer capacitance with a larger effective surface area as ion-accessible path channels for the rapid motion of electrons inside this mesoporous structure.

However, hollow alginate/graphene microfibers demonstrated more IR at $j=0.5$ A/g by adding graphene percentage from 0.25 % to 1.0 %, which resulted in the loss of porosity of generated hollow alginate/graphene microfibers. The discharging time obtained was longer than the charge time for samples containing graphene. The short circuits found in the developed microfiber electrode are associated with these charged capacitors discharging procedure. However, their related resistances could slightly increase the equivalent resistance of the whole system, which eventually led to a lengthened time in discharging according to the direct relationship between the discharging time and the equivalent resistance as follows:

$$V_c = V_s \left(1 - e^{-\frac{t}{RC}}\right) \quad \text{Eq. 1}$$

Where V_c is the voltage across the capacitor, V_s is the supply voltage, t is the elapsed time since the application of the supply voltage, R is the Internal resistance, and C is the capacitor capacity.

IV. CONCLUSION

In this study, electrically conductive hollow alginate/graphene composite microfibers were fabricated for the first time using a microfluidic approach. Fiber morphology, conductivity, and other features were studied under various flow rate ratios and graphene concentrations. According to obtained results, 200.0: 450.0: 230.0 $\mu\text{L}/\text{min}$ (sheath: core: sample) and 0.25% were chosen as optimum FRR and graphene concentration points, respectively. In conclusion, microfluidic technology could successfully confirm itself as a functional approach for fabricating electrically-conductive hollow alginate/graphene microfibers with about ten times more conductivity than hollow alginate microfibers with similar controllable size and shape compared to other fiber preparation techniques. Moreover, this work may open up more opportunities for such hollow alginate/graphene microfibers having significant potential to be employed in various areas such as energy, biomedical applications, and single-cell analysis. Future work could include the study of these hollow alginate/graphene microfibers potentials in the development of hollow microvessel fibers according to current requirements in specific physiological hollow microvessel and tissue engineering.

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Conflicts of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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Figure legends:

FIG. 1. Illustration of the microfluidic procedure for fabrication of hollow alginate/graphene microfibers using a five-channel microfluidic device.

FIG. 2. Study of dependency of hollow dimensions of alginate microfibers to sheath-to-core flow rate ratios. These results were obtained under 0.50, 0.44, 0.40, and 0.33 FRR, and data are presented as the mean of five measurements (\pm SD). The polymer flow was kept constant at 230.0 μ L/min.

FIG. 3. Scanning Electron Microscopy (SEM) images depicting the morphology of the hollow (a) alginate and (b) alginate/graphene microfibers manufactured by optimum FRR.

FIG. 4. DSC thermograms of hollow alginate and alginate/graphene microfibers.

FIG. 5. FT-IR spectra of developed hollow alginate and alginate/graphene microfiber.

FIG. 6. (a) Characterization of the alginate hollow microfibers contained a different amount of graphene through CV method in the potential range from -1.0 to +1.0 V (vs. Ag/AgCl) and at a scan rate of 10.0 mV s⁻¹. (b) Electrical behavior of conductive alginate/graphene hollow microfibers at various scan rates (10.0 – 2000.0 mV s⁻¹).

FIG. 7. (a) Nyquist plots of the prepared hollow fibers in the frequency range from 100 kHz to 0.01 Hz. (b) Galvanostatic charge/discharge curves of the alginate and hollow alginate/graphene microfibers series at the current density of 0.5 A g⁻¹.