

Block Copolymer Derived Porous Carbon Fiber for Energy and Environmental Science

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ABSTRACT

As the world population grows, a persistent pressure on natural resources remains. Resource requirements have extensively expanded due to industrialization. Several technological advancements continually aim to alleviate these resource shortages by targeting existing shortcomings in effective and efficient material design. Practical, high-performing, and economical materials are needed in several key application areas, including energy storage, energy harvesting, electronics, catalysis, and water purification. Further development into high-performing and economical materials remain imperative. Innovators must seek to develop technologies that overcome fundamental limitations by designing materials and devices which address resource challenges.

Carbon serves as a versatile material for a wide range of applications including purification, separation, and energy storage owing to excellent electrical, physical, and mechanical properties. One-dimensional (1D) carbon fiber in particular is renowned for excellent strength with high surface-to-volume ratio and is widely commercially available. Although an exceptional candidate to address current energy and environmental needs, carbon fibers require further investigation to be used to their full potential. Emerging strategies for carbon fiber design rely on developing facile synthetic routes for controlled carbon structures. The scientific community has shown extensive interest in porous carbon fabrication owing to the excellent performance enhancement in separation, filtration, energy storage, energy conversion, and several other applications. This dissertation both reviews and contributes to the recent works of porous carbon and their applications in energy and environmental sciences. The background section shows recent development in porous carbon and the processing methods under investigation and current synthetic methods for designing porous carbon fibers (PCF). Later sections focus on original research.

A controlled radical polymerization method, reversible addition-fragmentation chain transfer (RAFT), enabled a synthetic design for a block copolymer precursor, poly(methyl methacrylate) (PMMA) and polyacrylonitrile (PAN). The block copolymer (PMMA-*b*-PAN) possesses a unique microphase separation when electrospun and develop narrowly disperse mesopores upon carbonization. The PMMA and PAN domains self-assemble in a kinetically trapped disordered

network whereby PMMA decomposes and PAN cross-links into PCF. The initial investigation highlights the block copolymer molecular weight and compositional design control for tuning the physical and electrochemical properties of PCF. Based on this study, mesopore (2 – 50 nm) size can be tuned between 10 – 25 nm while maintaining large surface areas, and the PAN-derived micropores (< 2 nm). The mesopores and micropores both contribute to the development of the unique hierarchical porous carbon structure which brings unprecedented architectural control. The pore control greatly contributes to the carbon field as the nano-scale architecture significantly influences performance and functionality.

The next section uses PCF to clean water sources that are often tainted with undesirable ions such as salts and pollutants. Deionization or electrosorption is an electrochemical method for water purification *via* ion removal. I employed the PCFs as an electrode for deionization because of their high surface area and tunable pore size. Important for deionization, the adsorption isotherms and kinetics highlight the capacity and speed for purification of water. I studied PCF capacitive filtration on charged organic salts. Because PCF have both micropores and mesopores, they were able to adsorb ions at masses exceeding their own weight. The PFC adsorption efficiency was attributed to the diffusion kinetics within the hierarchical porous system and the double layer capacitance development on the PCF surface. In addition, based on the mechanism of adsorption, the PCFs showed high stability and reusability for future adsorption/desorption applications. The PCF performance as an electrosorption material highlights the rational design for efficient electrodes by hierarchical interconnected porosity.

Another application of PFCs is updating evaporative desalination methods for water purification. Currently distillation is not widely used as a source of potable water owing to the high cost and energy requirement. Solar desalination could serve as a low-cost method for desalination; however, the evaporation enthalpy of water severely limits practical implementation. Here I apply the pore design of PCF as a method for water nano-confinement. Confinement effects reduce water density and lowers evaporation enthalpy. Desalination in PCF were studied in pores < 2 nm to 22 nm. The PCF pore size of ~ 10 nm was found to be the peak efficiency and resulted in a ~ 46% reduction in enthalpy. Interestingly, the PCF nano-confinement also contributed to the understanding in competing desorption energy for evaporation in micropores. The pore design in PCF also shows confinement effects that can be implemented in other environmental applications.

Lastly, the block copolymer microphase morphology was explored in a vapor induced phase

separation system. The resulting PCF properties showed a direct influence from the phase separation caused by nonsolvent. At low nonsolvent vapor, a disordered microphase separation occurred, however upon application of nonsolvent vapor, the polymer chains reorganized. The reorganization initially improved mechanical properties by developing more long-range ordered graphitic chains in the PAN-derived carbon. However, at higher nonsolvent vapor concentrations, the fibers experienced polymer precipitation which resulted in bead and clump formation in the fiber mats. The beads and clumps lowered both mechanical properties and electrochemical performance. The vapor induced phase separation showed a method for enhancing mechanical properties without compromising electrochemical performance in flexible carbon fibers.

Block Copolymer Derived Porous Carbon Fiber for Energy and Environmental Science

Joel Marcos Serrano

GENERAL AUDIENCE ABSTRACT

Nanomaterials possess mechanical, physical, and electrical properties to address important growing demands for precious resources such as clean water and energy. Many advancements in nanomaterials focus on improving fine-tune architectures which facilitate efficiency in composites, filtration systems, catalytic systems, energy storage devices, and electronics. Carbon material has remained a valuable candidate in these fields owing to its abundance economical cost, and excellent properties. Several carbon forms provide unique characteristics including 0D dots, 1D fibers, 2D sheets, and 3D monoliths. Of these, 1D fibers possess excellent strength, resiliency, and conductivity and have been commercially employed in modern automotive, airplanes, membranes, and conductors. However, traditional carbon fiber fabrication does not match the growing needs in performance. Therefore, in this dissertation I explore the design and processing of carbon fibers for controlled architectures. These designs were then systematically studied in filtration systems, solar desalination, and flexible electronics.

Block copolymers provide a new way to combine polymers for drastically new materials and effects. Firstly, I conducted a comprehensive study on the synthesis and composition of this block copolymer which laid the foundation for future carbon fiber design. The polymer consists of two chains – one chain to develop carbon structures upon heating; the second which decomposes into pores upon heating. Therefore, with these two chains, a highly porous carbon fiber can be created. The reaction I studied could mostly be controlled with time to change the length of each chain. Ultimately, the pore size and surface area depend on the relative lengths of each chain. Future studies, including ones in this work, could therefore tune pore size and surface area for many applications.

Carbon fibers with graphitic structure are inherently conductive and thereby attract charged molecules in a solution. Diffusion and capacity serve as major factors in these types of systems. With the aforementioned control of the carbon fibers a diffusion study was conducted with charged pollution ions. Owing to the conductive nature, a voltage supply was attached to the fibers, which would adsorb ions electrostatically, termed “electrosorption”. The electrosorption performance within the carbon fibers elucidated the interconnected porous structure and how ions orientate

themselves along the surface of the fibers. In addition, with the development of ion orientation along the surface of the fibers, a greater than 1:1 ratio of carbon weight to ion weight adsorbed developed owing to the diffusion and ion stacking capabilities. Additionally, the study provides deeper investigation into movement of ions within confined nano-porous material.

The ever-growing need for renewable resources such as fresh water has pressured development into more efficient material. Solar desalination has attractive qualities which makes it a focus for micro-scale studies. One of the major limitations lies in the high energy input change liquid water into vapor. At 100 °C for boiling, desalination lacks sufficient efficiency for large-scale applications in evaporation. However, by utilizing nano-scale material, the fundamental properties of water can be altered. The carbon fibers were then created with various nano-pore sizes which revealed nano-confinement effects when subject to solar heating. With the shrinking of pore sizes, the density of water also decreased. A lower density means less energy was required to convert water from a liquid to a vapor state. The carbon fibers helped reveal real applications into confinement effects on water based on pore size. Apart from just desalination, this means future environmental application can utilize this knowledge for more effective and smart designs.

The carbon fibers outstanding electrical and mechanical properties have spurred research and development since the mid-1900s. Since then, carbon fiber technologies have grown from facile and efficient productions means, to high end, high performance smart design. The work presented here furthers two major components: first, the high-performance design of porous carbon fiber; second, the fundamental principles in nano-material properties and their applications. By first constructing a design of polymer synthesis and then subsequent studies, development of nano-porous carbon energy progresses knowledge on smart and efficient designs. These materials provide a platform for future energy and environmental sciences.

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Attributions

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Chapter 2. Tianyu assisted in design and execution of the electrochemical characterization. Assad U. Khan provided insights and meaningful edits during the writing process. Brandon Botset assisted in synthesis of the block copolymer. Benjamin J. Stovall provided polymer characterization. Zhen Xu, Ke Cao, Xi Hao, and Dong Guo assisted in data analysis and data curation. Shengfeng Cheng assisted with conceptual knowledge of the block copolymers.

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Chapter 1. Introduction to Porous Carbon for Energy and Environmental Science

1.1 Introduction

Several key issues arising from natural resource needs have spurred development in materials and devices with enhanced electrical, mechanical, physical, and chemical properties. Carbon-based materials serve as an excellent candidate owing to its abundance, economical production, versatility, strength, and electrical conductivity.¹ Carbon has also been shown over recent decades the successful implementation into devices, composites, and systems with specialized characteristics and architectures.² Among the various architectures of carbon, 1D tubes/fibers have been distinguishable for mechanical performance and surface area.³ For example, Damascus steel forged centuries ago was renowned for strength and quality. Recently Damascus steel was found to contain carbon nanotubes which forged various nano-fiber formations.⁴ Newer technologies expand the unique formation of carbon fibers aimed at addressing efficiency and properties.

Several discoveries for state-of-the-art carbon materials for energy and environmental sciences require controllable architectures, increased surface areas, and porosity.⁵ Carbon fiber development has been shaped by new precursor systems, fabrication, processing, and post-synthetic modification. Carbon sources diversly range from biomass sources such as food waste, plant product, *etc.* to petroleum derived synthetic polymers.^{6, 7} Carbon source research focuses on selecting and improving the carbon precursor which imparts important carbon fiber properties. Typically, precursor selection relies on four resulting carbon components: heteroatomic doping, graphitic crystallinity, carbon yield, and porosity. Poly(acrylonitrile) (PAN) which was first synthesized in the 1900s, provides pristine carbon fibers that exhibit these components except porosity.⁸ Porosity remains a key element developing more efficient energy storage, purification, and light-weight composites.

Currently fabrication processing aims at improving the surface area and porosity of carbon fiber without compromising desirable properties. Hard-template methods have produced excellent carbon fiber arrays, however, typically require caustic and dangerous removal

processes (HF, concentrated HCL, *etc.*).^{9, 10} Soft template methods employ surfactants that are less rigid but require safer removal processes. Soft template methods however demand compatible components which can solidify the carbon regions prior to decomposition of the soft material.¹¹ As an alternative, self-assembly methods allow a simpler and more direct approach toward pore generation.¹² Certain copolymers develop self-assembly systems depending on the microphase separation. PAN structure consists of a vinyl group linked to a nitrile functional group. The vinyl bond allows targeting for controlled radical polymerization with other vinyl monomers. Copolymerizing PAN with a sacrificial block allows self-assembly and a direct, facile PCF synthesis.¹³ Sacrificial blocks include soft polymers which decompose upon chemical or thermal treatment. Since PAN processing involves a carbonization step, the thermal decomposition allows a two-in-one processing. However, the activation levels of monomers also determine compatibility for polymerization given certain polymerization mediators. Mediators such as thiobenzoate have promising control and low dispersity and are compatible for both poly(methyl methacrylate) (PMMA) and PAN.¹⁴ Thiobenzoates allow for reversible addition-fragmentation chain transfer (RAFT) copolymerization which gives distinct A-B block copolymers rather than random blocks. The formation of the fiber and processing also determines the microphase separation.

Several avenues for carbon fiber fabrication exist, all of which impart unique carbon architectures. Original research methods of laser ablation and arc discharge allow pristine small research scale fibers but have no able for scale up. Chemical vapor deposition is well studied and commercially available but has high labor and cost. Large-scale spinning such as solution-spinning allow roll-to-roll manufacturing, but often only develop low surface area-to-volume ratios with large micron size fibers and require large nonsolvent coagulation baths. Electrospinning however allows spinning of fibers with $< 1\ \mu\text{m}$ diameters without a need for coagulation baths. Electrospinning polymer precursors for carbon fibers also gives the ability to develop hierarchical porous networks. These networks are a direct link to developing needed characteristics in advanced energy and environmental science materials.

1.2 Literature background

1.2.1 Carbon sources

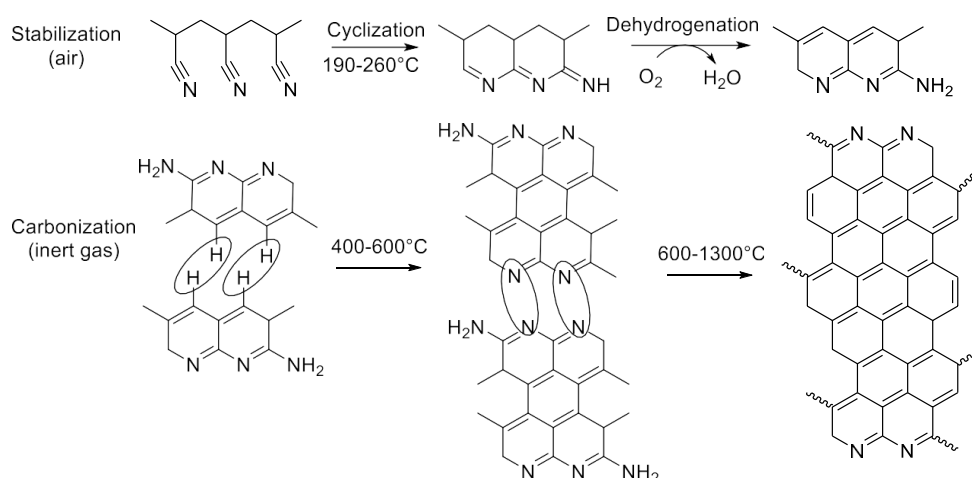
Carbon naturally occurs in abundance arising in many sources such as elemental carbon, biomass derived carbon, and synthetically derived carbon (**Table 1.1**). Elemental carbon sources such as coal, diamonds, pitch, and graphite exhibited the wide range of carbon formation and functionality. However, the structure of these carbons remains difficult to modify for targeted properties for energy and environmental sciences. Biomass carbon represents a wide range of sources including food waste and plant derived polymers including regenerated cellulose (rayon).¹⁵ Common examples are nut shells, bamboo stems, olive stones, seeds, flowers, coconut shells, seaweed, tobacco stems, and coffee grounds; each source provides different structural properties.¹⁶ As an abundant feedstock, the renewable biomass sources benefit from the lignocellulosic availability found in most parts of the world. However significant efforts are underway for lignin valorization.¹⁷ Particularly, for carbon products lignin, despite the cheap source, has not replaced more synthetic carbon sources due to low yield and composition. Unlike synthetic materials, modifications of these carbon sources are limited. Therefore, synthetic sources are used to obtain tailored carbon due to the tunability of polymerizations.

Table 1.1. Porous carbon sources, rayon (regenerated cellulose), Biomass, pitch, poly(ethylene) (PE), poly(vinyl acetylene) (PVA), and poly(acrylonitrile) (PAN). The common characteristics, pros, and cons are displayed.

Carbon sources	Characteristics	Pros	Cons	Ref
Rayon	from regenerated cellulose	well-studied	energy intense production	18
Biomass	many precursors	renewable source	low tunability; low yield	19
Pitch	economical	high carbon yield	petroleum impurities	20
PE	economical	abundant source	arduous processing; low carbon yield	21
PVA	poorly studied	alternative to synthetic precursors	poor yield & properties	22
PAN	readily available	high carbon yield	moderate cost	23

Synthetically derived carbon included pitch, poly(ethylene) (PE), poly(vinyl acetylene) (PVA), and poly(acrylonitrile) (PAN). Pitch represents an agglomeration of distilled carbon

sources generally including crude oil, coal, and some organic waste which result in limited carbon yield and impurities. Both PE and PVA have been studied as precursors for carbon fibers, however the current carbon yields mitigate any potential large-scale application. Whereas the high carbon yield, cross-linking abilities, electrical conductivity, and high mechanical strength of PAN has garnered interest in both research and industrial applications (**Scheme 1.1**). PAN first synthesized in the early 1900s, became popular once industrially available solvents were developed by DuPont in the 1940s.⁸ PAN has been used due to the high carbon yield (up to 56% in air and 80% in N₂).²⁴ The high char yield is due to the formation of stabilized graphitic structure developed during cross-linking of PAN. The thermal degradation of PAN allows a graphitic structure to develop amongst the carbon matrix, which in turn provides high strength in the fibers. However, for PAN-derived carbon fibers, modification is necessary to enhance their application in energy and environmental sciences.



Scheme 1.1. The oxidative crosslinking of PAN develops the ladder structure, and the subsequent pyrolysis at high temperature yields nitrogen-doped carbon.⁸

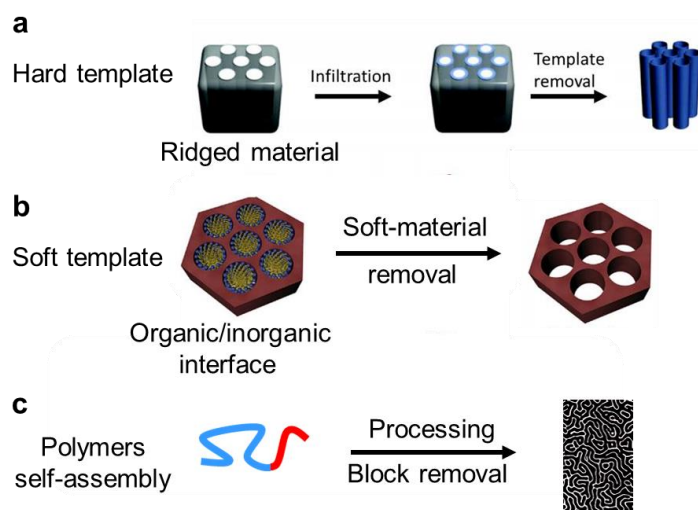
Improving desirable properties in PAN-derived carbon fiber necessitate controlled fabrication methods. Porosity serves as a method for enhancing light weight composites, energy storage devices, and purification systems.²⁵ Several methods for developing pores within nanomaterial have been developed over the past few decades.²⁵ Most commonly, pores arise from development of carbon sites, and vacancy sites. Synthetic methods utilize templating components as the vacancy generation, although the removal process strongly dictates the

efficiency in developing porous carbon.

1.2.2 Synthetic methods

Synthetic approaches to developing carbon-based material has evolved over the years to achieve varying architectures. In many applications, porous carbon exhibits advantages properties such as reduced weight, increase surface area, and more edge sites which are attractive for electrical components, structural components, and catalytic activity. Synthetic polymers are tunable for creating porous networks. Templating serves as the most abundant pathway for pore generation in carbon material. Synthetic carbon precursors are compatible with hard template, soft template, and self-assembly methods (**Scheme 1.2**).²⁶

Templating methods allow for developing arranged and aligned nanostructure arrays. Hard templatemethods typically use solid substrate and subsequently infiltrate monomer or polymer to create the nanostructures and requires a template removal process.²⁷ Hard templating requires nanostructures of firm material such as zeolite, silica, and metal oxides (commonly anodic aluminum oxide (AAO)).²⁸ Other hard templates include silica, metal oxides, salts, ice, organic, and bacterial templates.²⁹ The control of the AAO template allows for size-dependent studies with a vast number of polymers and polymer-based composites.³⁰ AAO has successfully shown ordered pore arraigments with various morphologies such as nanoparticles, nanofibers, and complex hybrid structures.³¹ Most hard templates must be removed with corrosive, hazardous chemicals including sodium hydroxide, hydrofluoric acid, and concentrated hydrochloric acid.^{32, 33} Alternatively soft templates which are often formed with surfactants, polymers, or micelles, typically require less toxic removal methods such as aqueous wash, thermal treatment, and freeze-drying.³⁴ Soft templates typically satisfy the nanostructure assembly into micro- or meso-pores but also cannot decompose prior to carbon precursor solidification.³⁵ Though the nanostructures require meticulous tuning for template uniformity, interface compatibility, orientation, and alignment which renders many soft-templates as non-scale.³⁶ The other templating route is self-templating or self-assembly.



Scheme 1.2. Templating methods, a) Hard template method often involves infiltration and polymerization of a material with subsequent removal of the template to develop arrays. b) Soft template has tantamount mechanisms and the original template is developed from surfactants. c) Polymer self-assembly materials rely on microphase separation and subsequent processing for block removal.

The self-assembly method has gained popularity due to the facile implementation, lack of arduous removal processes, and direct approach.³⁷ Most synthetic template-free systems rely on self-assembly and phase separation to create nanostructures. Self-assembly frequently relies on either the development of polymer microphase separation, or *in situ* components found in the precursor materials, such as biomass sources.^{38, 39} For biomass precursors, an eclectic variety has been discovered ranging which imparts unique characteristics from each source. However, the characteristics of the biomass-derived carbon are rarely tunable or controllable in significant ways. Therefore, unless the precursor material exactly matches the desired resulting carbon. Polymer-self-assembly methods for porous carbon remain understudied owing to the recent advancements in controlled polymerizations and polymer architectures.⁴⁰ Resulting porous carbon material typically arises from the polymer self-assembly. Polymer self-assembly allows parameters including, molecular weight, composition, solvent, etc. to change the microphase separation.⁴¹ The microphase separation relates the functionality and porosity of resulting carbon through more fine-tuned control. Synthetic template-free techniques avoid template fabrication, forgo caustic removal processes, and allow for highly control fabrication.⁴²

1.2.3 Porous carbon fabrication

Developing arrays structures and pores has been an imperative factor with the rise in nanomaterials. Several methods provide avenues for carbon fiber fabrication including arc discharge, laser ablation, chemical vapor deposition (CVD), solution-spinning, and electrospinning (**Table 1.2**). Of these, laser ablation⁴³ and arc discharge⁴⁴ provide good laboratory scale samples, but remain archaic, non-scalable, and limited in morphological control. CVD allows for high-end porous carbon development, although direct CVD research has been stagnant due to the high cost to production volume ratio. Solution-spinning represents a common method for large-scale carbon fiber production but limits morphological control and fiber diameter. Electrospinning contrastingly, shows lower yields for carbon fiber than solution-spinning, but allows for facile control of fiber diameter and morphology.

Table 1.2. List of porous carbon nanofiber fabrication methods with main characteristic, pros, cons, and most relevant reference to this literature review.

Fabrication Method	Characteristics	Pros	Cons	Ref
Laser ablation	High energy production of laser & starting material	Excellent array structures	Low control; Not scalable; low yields	43
Arc discharge	Plasma release in chamber to grow carbon	Highly pure samples	No large-scale production; limited starting material; slow	44
CVD	Growth seeding on carbon matrix	Fast, well studied	Expensive; labor intensive	45
Solution-spinning	Common large-scale production	High yield with good mechanical properties	Limited morphology control; no small fiber diameter	46
Electrospinning	Economical	Facile; controlled	Limited yields	47

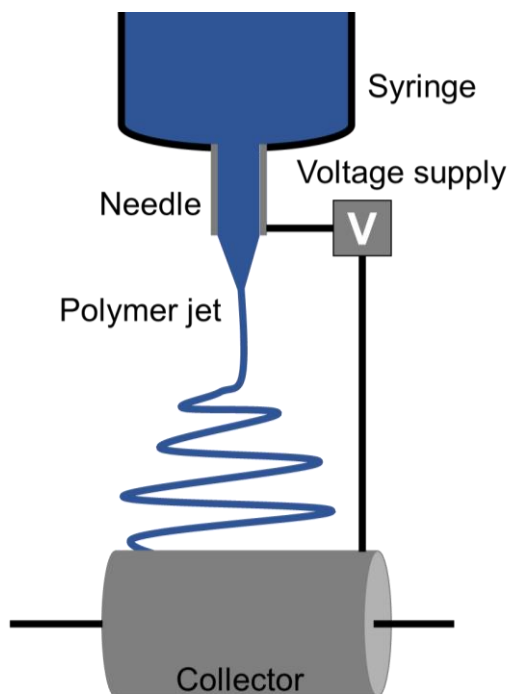
For tailored control and uniformity of membranes and electrodes, CVD has proven to be a reliable method though more expensive than spinning methods through high installation cost

and high maintenance costs. CVD produces uniform porosity and interconnectivity.⁴⁵ Briefly CVD uses a high vacuum chamber with an active material which is deposited onto a substrate.⁴⁸ CVD methods use catalyst growth, thermal CVD, or plasma enhanced CVD.⁴⁹ Catalyst growth CVD requires delicate purification processes to remove metal catalysts which adversely affect PCF.⁵⁰ Additionally, the vacuum chamber size also serves as the limiting factor for length of carbon fibers by CVD.⁵¹ More frequently, CVD produces carbon nanotubes which fit into the vacuum chamber. Overall CVD is an effective method at developing thin membranes and carbon nanotubes for many applications, but the complexity and expenses deter many innovations.

Polymer spinning for fiber fabrication involves either melt-spinning or solution-spinning. Broadly, melt-spinning remains a rapid fiber fabrication method for thermoplastics whereas thermosets are often used in solution-spinning. PAN is a thermoplastic; however, the PAN decomposes before reaching its melting temperature, so solution-spinning is often used. Solution-spinning requires a dissolved polymer of desirable viscosity and extrude it into a coagulation bath directly (wet-spinning) or with an airgap from the spinnerets tip to the coagulation bath (dry-spinning). Wet-spinning accounts for the majority of PAN produced carbon fiber. In addition, wet-spinning allows for PAN combination with various components for doping and pore generation. Polymer blends including synthetic and biomass derived polymers which share compatible solvents with PAN allow enhancement of carbon fiber properties. Porous carbon fibers from wet-spinning have garnered interests for achieving porosity through phase-separation, activation, polymer blends. However, wet-spinning carbon fiber precursors limit the diameter achievable and precise pore control remains challenging owing to the wet-spinning solvent/nonsolvent mechanism. The polymer solidification dictates the micro-structures of the resulting carbon fibers. The coagulation bath mechanism allows PAN reorganization into large domains given PAN immiscibility. Other spinning methods such as electrospinning cause rapid solvent evaporation and requires no coagulation bath. This mechanism allows for precursors assembly through more kinetic than thermodynamic pathways.

The first principles of electrospinning might have been realized in 1882,⁵² however implementing the method gain more momentum in the late 20th century with the raise of nanotechnology and nano-characterization methods. Since then, a boom of research highlights

the use-case in a vast variety of fields including in tissue regeneration scaffolds, wearable electronics, and composites. As a simple set-up involving a syringe, needle, high-voltage source, and grounded collector electrospinning exceeds CVD in affordability and no coagulation bath like solution-spinning. Importantly, electrospinning controls. Continuous fibers with these controlled diameters are achieved by the electrostatic repulsive force from the applied electric field (**Scheme 1.3**). With exposure to an electric field, polymer droplets deform into a Taylor cone and subsequently fibers owing to surface tension and electrostatic repulsion. This occurs at short time periods (< 50 ms) which is faster than other fiber solidification rates. The short time frame regulates microphase separation in polymer systems distinctly from other spinning techniques. Electrospinning addresses several challenges for high performance material without sacrificing effective surface area and maintaining a low operation cost.



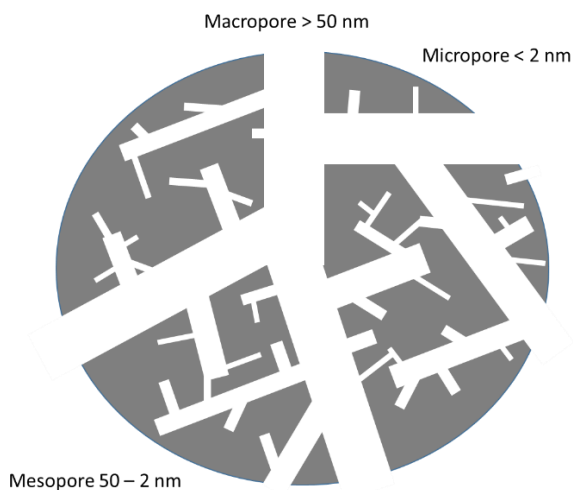
Scheme 1.3. Electrospinning system scheme, electrospinning with syringe injection, DC voltage supply, and grounded collector.

1.3 Carbon based energy storage

Growing energy demands have inspired development in efficient, lightweight, and power-dense material. Supercapacitors represent electrochemical devices which possess superior cycle life

and high-power density required in energy storage, and electronics. Supercapacitors optimization to serve in these roles focus on improving electrical double-layer capacitance, and pseudo-capacitance.^{53, 54} Enhancing double-layer capacitance and pseudo-capacitance requires the development of specific surface area and heteroatomic doping. Significant work in porous carbon-based materials represent excellent progress in supercapacitors.^{55, 56}

The hierarchical porous structures mitigate the complications of diffusion resistivity and surface area accessibility.⁵⁷ Larger pore sizes lack possess high volume to surface area ratio whereas smaller pores often become encapsulated by carbon thus rendering them inaccessible. However, by having a hierarchy of macropores (> 50 nm) mesopores (2-50 nm) and micropores (< 2 nm) the desired surface area and low diffusion resistance can be achieved (**Scheme 1.4**). This pore structure creates accessibility within the voids for electrolyte penetration and high effective surface area.⁵⁸⁻⁶⁰

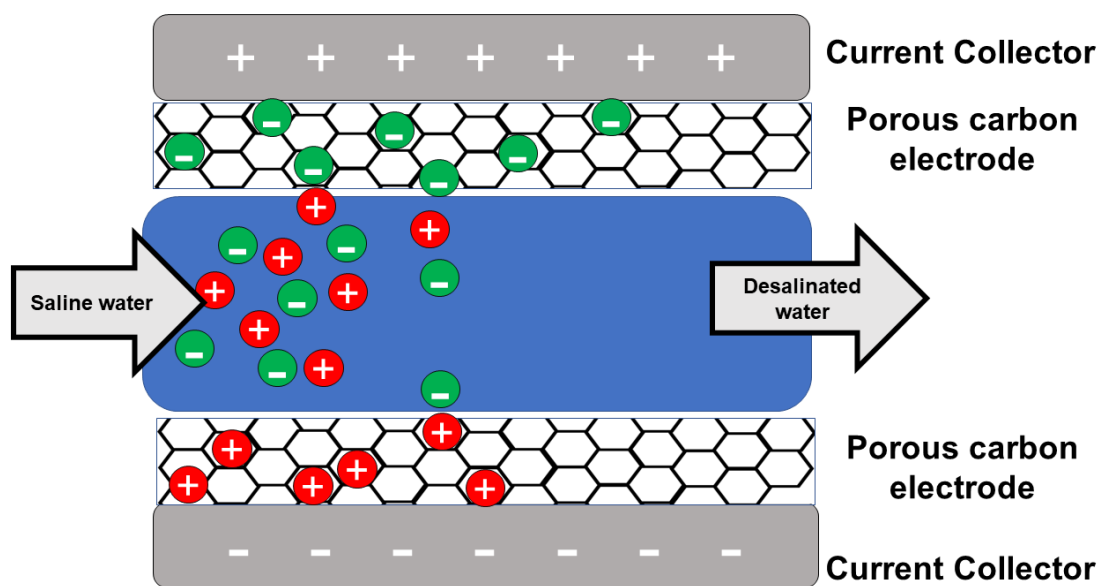


Scheme 1.4. Flow of hierarchical interconnected porosity of material from macropores to micropores.

1.4 Porous carbon for capacitive deionization

The scarcity of potable water grows larger and has been monitored by WHO/UNICEF who compiled a report in 2017 estimating 2.1 billion people lack access to safe and reliable water sources.⁶¹ Unfortunately, current technologies are unable to ameliorate the freshwater demands. Fresh water sources remain scarce and intermittent in availability. Salt water represents the

vast majority of water on earth. With only a fraction of fresh water available, while the majority resides in the ocean, many of these systems aim at developing energy efficient water harvesting. Some of the prominent desalination techniques under investigation show promising results including: reverse osmosis (RO),⁶² multi-stage flash (MSF),⁶³ multi effect distillation (MED),⁶⁴ capacitive deionization (CDI),⁶⁵ solar desalination⁶⁶. Historically acquisition from oceanic water proves too energetically costly. For each of these their relative energy consumptions has been characterized, and most of the these require high capital cost and moderate to high energy cost.⁶⁷ Therefore efficiency and reducing expenditure remains a forefront challenge. Systems such as RO, MSF, and MED require vast infrastructure and significant initial cost. Communities with the worst water available also lack resources to afford large water purification systems, therefore simpler and more efficient systems like CDI or solar desalination might address these specific needs.



Scheme 1.5 Overview of capacitive deionization. Water flows across the diagram, saline water enters between a porous cathode and anode which captures the respective ions. The electrosorption is a characteristic of the capacitance of the electrode material.

Capacitive deionization has been on the rise with recent development carbon-based electrodes with sufficiently high double layer capacitance.⁶⁸ Specifically, electrosorption is the processes by which ions are adsorbed onto the conductive electrodes. These removal processes often

take the input of current, and the mechanism allows for high regeneration processes (**Scheme 1.5**). Typically, this includes undesirable ions which are absorbed onto the surface of the electrode. CDI systems often require a current collector attached to a high-surface-area electrode to build multiple layers of ions within the active material. Newly developed template-free synthesis has shown promising hierarchical structures for energy efficient alternatives.⁶⁹

CDI provides a platform for ion removal which typically overcomes fouling and reusability complications in other filtration systems.⁷⁰ Given the mechanism for CDI, the goal of the material development has been to increase capacitance and the effective surface area of the electrodes. Carbon based CDI allows for more heteroatomic doping, which allows for non-faradaic and pseudo-faradaic charging to occur which contributes to the ionic electrosorption of the active material.⁷¹ For carbon-based electrodes there are still efforts to decrease the required voltage and enhancing the physical absorption of ions.⁷² Typically a conflict exists between diffusion capabilities and high adsorption capacitance. Micropores mitigate the absorption capabilities by bulky ions detrimentally increasing diffusion resistance, whereas macropores allow good diffusion but a low specific surface area. In order to provide a platform for high diffusion and high capacity, the use of hierarchical pores provides a system to both infiltrate and retain material. Specifically, the ability to investigate the diffusion of aqueous solutions within a conductive carbon network of multiple pore sizes opens the field to other confinement effect systems.

1.5 Porous carbon for desalination

Several technologies have risen as sustainable alternatives with porous technology including direct and in-direct solar based desalination systems (**Fig. 1.1**).⁷²⁻⁷⁴ Other desalination methods are expensive, need high energy input, and require heavy industrialization.^{51, 71, 75} Currently research has afforded massive innovations in energy harvesting as solar plants are being implemented. However solar desalination technologies are lacking and fail yield large amounts of fresh water. Therefore, several solutions for solar desalination have been explored including solar heat pumps, nanoparticles, biomass derived carbons, and carbonized materials. In order to provide a means for solar desalination to overcome current desalination systems, the

fundamental properties of energy harvesting, and energy requirements need to be addressed.



Figure 1.1 Solar technologies overview. These technologies have been growing due to increased efforts for sustainable energy sources. Although several voltage innovations have been created, there's a stark lack of economical large-scale implementation. Currently ponds and stills are being developed though they are limited in freshwater output. Adopted from Ref.⁷⁶

Solar desalination devices specifically target the two key properties: 1) reducing the enthalpic energy required to vaporize water, and 2) localizing solar energy to a boundary (substrate/water or water/air) to increase heat transfer to water molecules.⁶³ Reducing the enthalpic energy has been achieved in several ways. One of which is confining water molecules to a nano sized compartment which changes the physical properties. By reducing the hydrogen bonding of bulk water in <100 nm droplets and having a phase barrier (air/water interface) enthalpic energy for vaporization is lowered.⁷⁷ This has been applied by porous materials, which is typically carbonized to absorb solar radiation (**Fig. 1.2a**). Alternatively, plasmonic nanoparticles which absorb photons and transfer heat to thin water layers, allow for confined steam generation. As the steam is generated, the weight of the water is lower than the surrounding bulk water and bubbles up, escaping from the bulk water (**Fig. 1.2b, c**). There is merit to this method, but nanoparticle stability and scaling has not been successful. Since the nanoparticles are confined by size, the heat is already localized, however for larger materials this is achieved by isolating water to the water/air interface and sometimes including insulation materials (**Fig. 1.2d-f**). Therefore, alternative, scalable methods which utilize both key properties for efficient solar desalination are imperative to investigate.

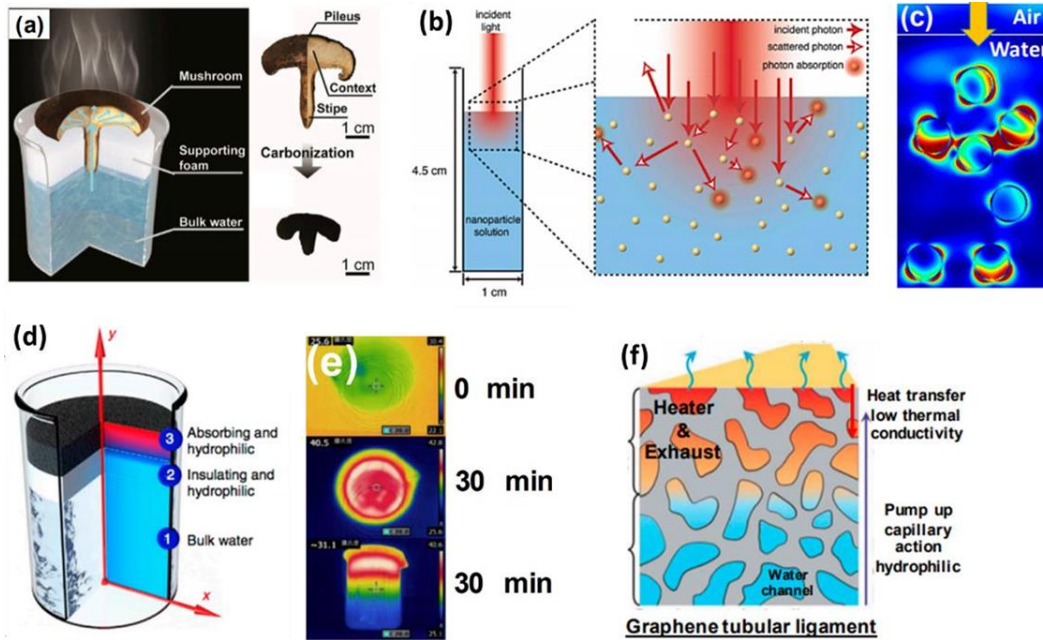


Figure 1.2 Innovative solar desalination materials. (a) A mushroom as a biomass carbon shows the capabilities for small scale desalination. (b) Nanoparticles currently are under research based on photon absorption and heating along the boundary of the nanoparticle. (c) Heat map of proposed nanoparticle steam aggregation. (d) Graphite material has potential in solar absorption as a black body to heat the interface of water and air where (e) the heat can be localized (infrared image). Typically, this occurs by a porous material to channel water to the localized heat source. However, the overall focus of the field is a reduction of the enthalpic energy barrier for vaporizing water while simultaneously localizing the solar generated heat to the boundary between water and air. (Adapted from Ref⁷⁸⁻⁸²)

1.6 Porous carbon for structural electronics

Carbon fiber in commercially available material often serves as structural components since the graphitic nature provides high mechanical resiliency. Roll-to-roll production of carbon fiber has advanced beyond basic fiber production and includes various *in situ* functionality for applications from electrodes to composites.⁸³ Mechanical properties of solution-spun fibers show excellent mechanical properties, however the fiber size typically diminishes any electrochemical performance available to the fibers. Electrospinning often produces fiber sizes smaller than in

various solution-spinning methods, which lend towards lower mechanical properties. Electrospinning of block copolymers remain understudied for structural electronics. In addition, the flexibility often derives from a culmination of mechanical properties, free volume, and fiber-to-fiber structures.⁸⁴ however, the limited long-range architectures limit CNTs by the support material required in flexible devices.⁸⁵ Indeed some of the complications have been the difficulty in dispersion and locality.⁸⁶

Material design for structural electronics often combine mechanical and electrochemical performance. Extensive research into nanomaterial showed conductive material such as graphene sheets, nanowires, polymer fibers, organic films, and composites.^{55, 56, 87-89} Beyond the molecular structures for electrochemistry, the geometric development also plays a role in structural integrity.⁸⁵ Especially for low diminution material, the form of the material contributes to out of plane deformation. One direction for these has been carbon yarn with interior pores for deposition of pseudocapacitive compounds.⁸⁴ However, carbon yarn, and other fibers developed from solution-spinning are often larger in diameter and without significant pore structures. This leads towards the mechanical performance but then lacks in electrochemical properties. In addition, similar considerations for supercapacitors also exist for flexible electronics, however with the addition of deformation during use. For block copolymer-based carbon fiber, the morphological development of pores introduces both pore volume, surface area, and composition of graphitic carbon. Specifically, fields of electrospinning and methods from solution-spinning together might provide a combination of structural and electrochemical performance.

As mentioned before, phase-inversion and certain solution-spinning methods utilize various compositions of polymer/ solvent/ non-solvent systems to control resulting physical, mechanical, and electrochemical properties. Implementing block copolymers into an electrospinning system with inclusion of solvent/ non-solvent systems provides an increased perplexity to the system. Polymer membranes utilize vapor induced phase-separation (VIPS) in order to develop polymer crystalline structures which affect mechanical properties.⁹⁰ PAN electrospun material which retain both electrochemical and mechanical properties would allow advancement in flexible electronics.⁹¹ The introduction of other polymeric systems with PAN also means a whole new set of parameters for fabrication giving the microphase separation of the polymer. With new synthetic methods arising, there are new polymers which are being investigated for how environmental effects such as humidity (which can serve as either a solvent or nonsolvent) effect resulting

macroscale properties (**Figure 1.3**). By implementing both electrospinning, block copolymers, and VIPS new types of carbon fibers could give rise to advancements in structural/electrical components. These include components of electric vehicles, aerospace vessels, wind turbines, and so forth. Development of an efficient energy storage material which also possesses structural resiliency provides the ability to integrate energy and environmental necessities for advanced material design.

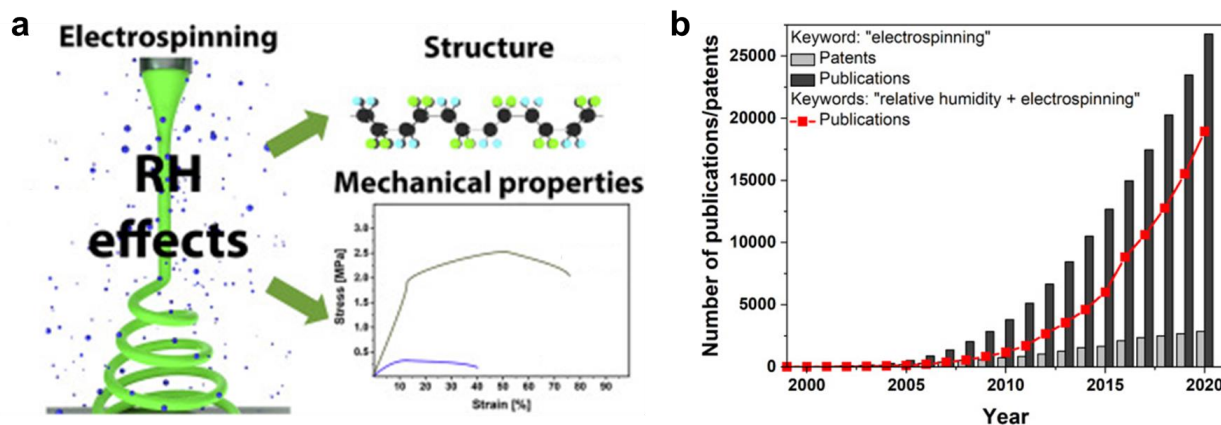


Figure 1.3 Relative humidity electrospinning overview. (a) Schematic display of electrospinning with relative humidity (RH) and how it may result in changes for structural and mechanical properties. (b) A systematic study of the number of publications related to “electrospinning”, and “relative humidity + electrospinning” from the year 2000 to 2020. Adapted from Ref ⁹².

1.7 Conclusions

Carbon fibers show excellent promise for applications in energy and environmental sciences. Although currently commercially available, the integration of carbon fibers into advanced energy devices (storage, acquisition, *etc.*) require development and control of nanoscale architectures. Based on the literature background presented, porous carbon fiber possesses physical and electrochemical properties which target high performance energy storage as well as purification techniques. The design of the pores along the nanometer scale provides an avenue to explore fundamental properties in both carbon fibers and nanoconfinement effects on solutions within the pores. The work herein therefore focuses on porous carbon fibers and their design to highlight the fundamental properties targeted in energy and environmental applied materials.

The chapters found in this dissertation flow from polymer design to application and physical/chemical phenomena probed using porous carbon fibers. The second chapter highlights the block copolymer precursor synthesis. This chapter explains the compositional design to target mesopores within the porous carbon fibers which will be used in later chapters. The third chapter continues the work of the first by studying the diffusion and isothermal adsorption of charged ions. The capacitive deionization exemplifies the purification properties of the carbon fibers using hierarchical porosity. The fourth chapter explores the nanoconfinement effects of salt water and the resulting desalination effects based on various pore sizes. Given the fundamental work of the first chapter, such physical phenomenon can be probed. The fifth chapter explores the microphase separation of the block copolymer based on vapor induced phase-separation. By introducing the humidity effects on polymer mobility during spinning, the resulting carbon fibers alter physical properties which allows further tunability and modification available for material design. The sixth and final chapter summarizes the culmination of work completed in this dissertation and provides prospects for furthering the field of porous carbon fibers.

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Chapter 2. Composition Design of Block Copolymers for Porous Carbon Fibers

This chapter has been adapted from a published manuscript by [J. M. Serrano](#), T. Liu, A. Khan, B. Botset, B. Stovall, Z. Xu, D. Guo, K. Cao, H. Xi, S. Cheng, and G. Liu from the following reference: **Chem. Mater.** 2019, 31, 8898. Reprinted (adapted) with permission from American Chemical Society. Copyright © 2019 Chem. Mater.

2.1 Abstract

Block copolymer-based porous carbon fibers (PCFs) exhibit hierarchical porous structures, high surface areas, and exceptional electrochemical properties. However, the design of block copolymer for PCFs remains a challenge in advancing this type of fibrous material for energy storage applications. In this chapter we have systematically synthesized a series of poly(methyl methacrylate-*block*-acrylonitrile) (PMMA-*b*-PAN) with well-controlled molecular weights and compositions to study the physical and electrochemical properties of PCFs. PCFs are synthesized *via* electrospinning, self-assembly, oxidation, and pyrolysis with no additives or chemical activation. By adjusting the molecular weights of PAN and PMMA blocks, we have achieved tunable mesopore sizes ranging from 10.9 to 18.6 nm and specific capacitances varied from 144 to 345 F g⁻¹ at 10 mV s⁻¹. Interestingly, regardless of the volume fraction of PAN, all block copolymers produce hierarchical porous structures due to the self-assembly and crosslinking of PAN. Block copolymers with a PAN volume fraction of near 50% show the highest surface areas and gravimetric capacitances. The PCFs represent a new platform material with tunable specific surface areas, pore sizes, and electrochemical properties. This work has an immediate impact on designing block copolymers to create PCFs for applications in energy conversion and storage.

2.2 Introduction

Carbon is a widely used supercapacitor electrode material because of the high electrical conductivity, chemical stability, and structural versatility.¹⁻⁶ Among various forms of carbon, carbon fibers are attractive because they offer continuous and rapid electron conduction that is essential for ultrafast charging and discharging. In addition to the high mechanical strength that enables their operation under extreme conditions, the self-standing nature eliminates the need for

polymer binders which increases electrical resistance.⁷ Similar to carbons in other formats, carbon fibers store electrical energy primarily by electrical double layers at electrode/electrolyte interfaces.⁸ Their surface areas, and pore size distributions are critical factors of ion-accessible surfaces and ion diffusion kinetics, both of which strongly influence capacitance and rate capability, the two figures-of-merit for supercapacitors.^{9,10}

In the last decade, porous carbon fibers have been synthesized from a plethora of precursors such as biomass (*e.g.*, coconut husk, pistachio shell, and banana peel),^{11–14} pitch,^{15,16} polyethylene,¹⁶ and polyacrylonitrile (PAN).¹⁷ The control over the porous structure, however, has been challenging. For example, the porosity of biomass-derived carbon fibers is predetermined by the biomaterials and lacks tunability. The variation in the biomass composition also leads to limited reproducibility of porous structures. Pitch and PAN-derived carbon fibers have pores mainly in the micropore range (<2 nm).^{18,19} The small micropores slow down ion diffusion and impede ion accessibility to internal pores, which significantly reduces the rate capability and capacitance.²⁰ Coupling hard templates,²¹ soft templates,^{22,23} or sacrificial polymers^{24,25} with pitch and PAN yields carbon fibers with meso- and macro-pores,^{26–28} but the pore-size uniformity and pore spatial distribution are poor due to non-uniform dispersion of the templates or sacrificial polymers in the carbon precursors.^{29–32} Moreover, the hard templates must be removed *via* additional steps after pore formation, rendering the synthesis processes arduous and time-consuming.

Recently, our group has developed a method for synthesizing porous carbon fibers (PCFs) with uniform mesopores and a narrow pore size distribution from poly(methyl methacrylate-*block*-acrylonitrile) (PMMA-*b*-PAN).³¹ The mesopore uniformity stems from the well-defined microphase separation of poly(methyl methacrylate) (PMMA) and poly(acrylonitrile) (PAN) into bicontinuous domains upon thermal annealing. The subsequent pyrolysis of PMMA-*b*-PAN decomposes PMMA and carbonizes PAN, resulting in uniform mesopores throughout each fiber. The method to some extent is similar to the direct use of block copolymers such as poly(acrylonitrile-*block*-butyl acrylate) (PAN-*b*-PBA) and poly(styrene-*block*-4-vinylpyridine) (PS-*b*-P4VP) to generate carbon powders and films with porous structures.^{33,34} One expects that varying the molecular weights of PMMA and PAN blocks alters the sizes of PMMA and PAN domains,^{31,35} and thus the mesopore size, pore volume, and surface area of PCFs after pyrolysis. However, all previous studies have focused on preparing porous carbon in the format of powders, particles, and monoliths. For example, block copolymers such as poly(styrene)-*block*-

poly(ethylene oxide) (PS-*b*-PEO) have been used to template the formation of mesoporous carbon nanospheres^{36,37} and nanocomposites.³⁸ The fibrous format of porous carbons requires drastically different polymer properties, and thus a systematic study of the block copolymer precursors is urgently needed to fully elucidate the conversion of block copolymers into porous carbon fibers. The foremost question is how to design block copolymer precursors of certain molecular weights and compositions to obtain specific structures and properties in porous carbon fibers.

In this chapter, we systematically study the interplays among the molecular weight and composition of PMMA-*b*-PAN, the porous structures of PCFs (surface areas, pore size distributions, and pore volumes), and the electrochemical performances of PCFs (impedance, gravimetric capacitance, and rate capability). We synthesized three series of PMMA-*b*-PAN with three number-average molecular weights (M_n) of PMMA (M_n = 39, 62, and 85 kDa). In each series, the PAN volume fraction (ϕ_{PAN}) was systematically increased from ~ 0.25 (PAN minor block) to ~ 0.5 (symmetric PAN and PMMA blocks), and to ~ 0.75 (PAN major block). Electrospinning and pyrolysis of PMMA-*b*-PAN yielded PCFs (Figure 2.1). Depending on the molecular weight and composition, the mesopore size of PCFs varied between 10.9 and 18.6 nm, and increased with decreasing ϕ_{PAN} . In each of the three series, block copolymers with $\phi_{\text{PAN}} \sim 0.5$ showed the maximum surface areas and gravimetric capacitances. Block copolymer with an intermediate molecular weight ($M_{n, \text{PMMA-}b\text{-PAN}} = 62\text{-}b\text{-}56$ kDa) achieved the maximal surface area of $918 \text{ m}^2 \text{ g}^{-1}$ and the highest gravimetric capacitance of 345 F g^{-1} at 10 mV s^{-1} .

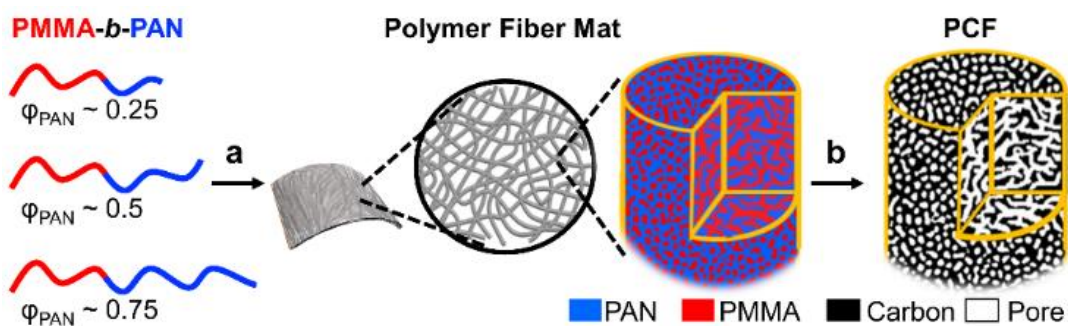


Figure 2.1. (a) PMMA-*b*-PAN of various molecular weights, and compositions are electrospun into a polymer fiber mat. The mat is zoomed in to illustrate the individual polymer fibers. (b) After microphase-separation into PAN (blue) and PMMA (red) domains, the block copolymer fibers are oxidized, cross-linked, and carbonized into porous carbon fibers. The block copolymer composition controls the pore size, surface area, and electrochemical performance.

2.3 Experimental Section

2.3.1 Materials

Acrylonitrile (AN, $\geq 99\%$), methyl methacrylate (MMA, $\geq 99\%$), 2,2'-azobis(2-methylpropionitrile) (AIBN, $\geq 98\%$), cumyl dithiobenzoate (CDB, $\geq 99\%$), benzene ($\geq 99.9\%$), aluminium oxide (activated, neutral, Brockmann Activity I), *N,N*-dimethylformamide (DMF, $\geq 99.7\%$), and dimethyl sulfoxide (DMSO, $\geq 99.9\%$) were obtained from Sigma-Aldrich. Methanol was used for polymer purification. Nickel foam was purchased from MTI (surface density = 350 g m^{-3}) and used as the supercapacitor electrode substrate. The monomers (AN and MMA) were passed through alumina columns to remove inhibitors prior to use. All other chemicals were used as received without purification. (average $M_w \sim 1,000,000 \text{ g mol}^{-1}$, powder) (434574), ascorbic acid ($\geq 99.0\%$ crystalline)

2.3.2 Synthesis of PMMA-*b*-PAN block copolymer

PMMA-*b*-PAN block copolymers of various molecular weights were all synthesized by reversible addition-fragmentation chain transfer (RAFT) polymerization. First, a mixture of MMA (35.0 mL, 309 mmol), CDB (84.3 mg, 0.309 mmol), and AIBN (25.4 mg, 0.155 mmol) were dissolved in benzene (51.6 mL) in a 100-mL Schlenk flask. The mixture was subjected to three cycles of freeze-pump-thaw (FPT) followed by back-filling with N_2 to remove the dissolved oxygen gas. Then, the flask was placed in an oil bath maintained at 60°C for 12 to 48 h to synthesize PMMA macro-chain transfer agents (CTAs) of different molecular weights: 39 kDa (12 h), 62 kDa (24 h), and 85 kDa (48 h). The resulting PMMA macro-CTAs were precipitated in methanol, filtered, and repeated twice. The resulting polymer was dried under vacuum for 12 h. The purified PMMA macro-CTA was used to synthesize PMMA-*b*-PAN block copolymers. PMMA macro-CTA (0.650 g, $10.8 \mu\text{mol}$), AN (2.60 mL, 43.3 mmol), AIBN (0.44 mg, $2.7 \mu\text{mol}$), and DMSO (7.22 mL) were mixed in a 40-mL Schlenk flask. The mixture was degassed by three FPT cycles and then heated in an oil bath at 65°C under N_2 atmosphere. The BCP blocks were prepared at various durations (10, 24, and 56 h) to obtain different volume fractions of PAN (Table 2.1). The PMMA-*b*-PAN block copolymers were purified following the same steps as PMMA macro-CTAs.

2.3.3 Preparation of PCFs

PMMA-*b*-PAN block copolymers were dissolved in DMF at a concentration of 16 wt%. The solution was stirred at 65 °C for 4 h and then electrospun into polymer fiber mats at a feeding rate of 1.8 mL h⁻¹ and under a voltage of 18 kV (Acopian Technical Company, Easton, PA). The polymer fibers were collected on an in-house-built rotary Al drum. Oxidization and pyrolysis of the fibers were conducted in a tube furnace (Lindberg/Blue M, Asheville, NC). The fiber mat was first oxidized by heating in air from room temperature to 280 °C at 1 °C min⁻¹ and isothermally stabilized at 280 °C for 8 h. After oxidation, the fiber mats were heated again from room temperature to 800 °C at a ramp rate of 10 °C min⁻¹, and maintained at 800 °C for 1 h under N₂ atmosphere (flow rate = 200 sccm).

2.3.4 Polymer characterization

Number average molecular weight (M_n) and polydispersity index (PDI) were measured *via* an EcoSEC HLC-8320GPC size exclusion chromatography (SEC) with a DynaPro Nanostar photometer and a light scattering detector. The mobile phase for the SEC was DMF containing 0.05 M LiBr. The flow rate of DMF was 0.5 mL min⁻¹ and column temperature was 50 °C. Each SEC trace consumed 100 μ L of 1 mg mL⁻¹ polymer solutions.

2.3.5 Physical characterization

Thermal gravimetric analysis (TGA) was performed on a Discovery TGA5500 (TA instruments) analyzer by heating samples from room temperature to 600 °C at a ramp rate of 10 °C min⁻¹ under ultrapure N₂ (flow rate: 25 mL min⁻¹). N₂ and CO₂ physisorption was conducted by a pore analyser (3Flex Pore Analyzer, Micromeritics Instrument Corp.) at 77 K and 273 K, respectively. Prior to the physisorption tests, all carbon fibers were heated at 90 °C for 60 min and then at 350 °C for 900 min in N₂ to desorb any moisture and hydrocarbons. The ramp rates of both heating processes were 10 °C min⁻¹. The surface areas were calculated using Brunauer-Emmett-Teller (BET) theory, and the pore size distributions were derived from non-local density functional theory (NLDFIT).³⁹ A field-emission scanning electron microscope (FE-SEM, LEO 1550) was used to acquire SEM images at an accelerating voltage of 2 kV and a working distance of ~3 mm. To make the oxidized polymer fibers more electrically conductive, a ~2-nm-thick layer of iridium

was deposited on the fibers using a Leica EM ACE600 sputter. Raman spectra were collected using a Raman spectrometer (WITec alpha 500) with a confocal microscope. The laser excitation wavelength was 633 nm. Deconvolution of the Raman peak was performed using Gaussian fit function of *PeakFit* software.

2.3.6 Electrochemical characterization

All electrochemical tests were performed using a PARSTAT 4000+ electrochemical workstation (Princeton Applied Research, AMETEK Inc.) with a three-electrode testing configuration. The working electrodes were made by sandwiching ~1 mg of PCFs between two pieces of nickel foam and pressed at 5 metric tons for 30 seconds. An Ag/AgCl electrode (in saturated KCl aqueous solution) and a piece of nickel foam were used as the reference and counter electrodes, respectively. The electrolyte was 3 M aqueous KOH solution for all electrochemical tests. Cyclic voltammetry (CV) and chronopotentiometry (CP) were carried out within a potential window from 0 to -0.8 V vs. Ag/AgCl. CVs were collected at various scan rates between 10 and 1000 mV s⁻¹ and CP tests were performed at 10 A g⁻¹. The CV gravimetric capacitances were calculated using the following equation,²⁹

$$C = \frac{1}{2(V_t - V_0)v} \int_{V_0}^{V_t} |I_m(V)| dV \quad (2.1)$$

where I_m (V) is the current density (A g⁻¹); v is the scan rate (mV s⁻¹); V_0 and V_t are the lower and upper potential limits of the potential window, respectively. Alternatively, CP capacitance was calculated using the discharging time (Δt),¹⁹

$$C = \frac{I_m \Delta t}{\Delta V} \quad (2.2)$$

Electrochemical impedance spectroscopy (EIS) was conducted between 0.1 Hz and 100 kHz with 10 mV perturbation at open-circuit potentials. The spectra were fit according to an equivalent circuit (Figure S2.1) using *ZSimpWin* software.

2.4 Results and Discussion

2.4.1 Synthesis and design of block copolymers

To design block copolymers for PCFs with hierarchical porous structures, we have synthesized three series of PMMA-*b*-PAN by RAFT polymerization with different polymerization times. The three series of PMMA-*b*-PAN are denoted as BCP 39-X, BCP 62-X, and BCP 85-X, with the numbers and X representing the number average molecular weight (M_n) of PMMA and PAN in kDa, respectively (Table 2.1). The target PAN volume fractions (ϕ_{PAN}) of the three block copolymers in each series are approximately 25%, 50%, and 75%. The molecular weights of all polymers were determined using SEC with a light scattering detector (Figure 2.2a-c). The SEC trace of each BCP showed a unimodal peak, indicating a relatively low polydispersity index ($\text{PDI} \leq 1.20$). As the PAN volume fraction was increased from ~ 0.25 to ~ 0.5 , and to ~ 0.75 in each series, the retention time was reduced, and the molecular weight of PAN block increased. The SEC traces of the block copolymers with the highest ϕ_{PAN} showed small tails at long retention times, indicating the presence of some low-molecular-weight polymers resulted from premature termination during polymerization.

Table 2.1. PMMA and PMMA-*b*-PAN block copolymer characteristics.

Designation	PMMA (kDa)	M_n PAN (kDa)	M_n PDI	ϕ_{PAN}	Char yield (%)
PMMA 39	39	-	1.02	-	0
BCP 39-13	39	13	1.16	0.25	27
BCP 39-36	39	36	1.10	0.47	33
BCP 39-149	39	149	1.20	0.79	37
PMMA 62	62	-	1.06	-	0
BCP 62-20	62	20	1.15	0.24	31
BCP 62-56	62	56	1.14	0.47	36
BCP 62-200	62	200	1.10	0.76	40
PMMA 85	85	-	1.10	-	0
BCP 85-40	85	40	1.17	0.31	35
BCP 85-60	85	60	1.20	0.41	40
BCP 85-215	85	215	1.16	0.71	45

The three series of BCPs were further characterized by TGA to evaluate the char yields and distinguish the composition variations. The TGA profiles revealed degradation temperatures and char yields similar to previous reports on PMMA/PAN blends and block copolymers.^{40,41} All the PMMA of different M_n showed nearly identical TGA profiles and were fully degraded at temperatures above 425 °C (Figure 2.2d-f). The TGA profile of PAN displayed a single weight-loss stage starting at ~270 °C, which was attributed to the degradation of PAN associated with formation of hydrogen cyanide, carbon dioxide, carbon monoxide, and other products.⁴² Beyond 320 °C, the continuous crosslinking and carbonization of PAN led to a gradual weight loss. The char yield was 72% for PAN with a molecular weight of 85 kDa, which was comparable to previously reported results for PAN.³¹ In contrast, the TGA profiles of BCPs showed three distinct weight-loss stages (Figure 2.2d-f). The first stage at ~280 °C was due to the dehydrogenation and cross-linking of PAN.⁴³ The second stage at ~325 °C portrayed the degradation of PMMA. The rapid weight loss during this stage was caused by the negligible char yield of PMMA. The TGA profiles plateaued at temperatures beyond ~475 °C and PAN was fully pyrolyzed into carbon. The char yields of the block copolymers increased with ϕ_{PAN} (Figure S2.2). Specifically, the char yield under an N₂ atmosphere increased ~4% as the molecular weight of PAN was increased from 39 to 62 kDa and from 62 to 85 kDa (Table S2.1 and Figure S2.2). At the same ϕ_{PAN} , the char yields also increased with the molecular weight of the PAN block. The higher char yields of higher molecular weight BCPs resulted from the more intensely cross-linked PAN.⁴⁴

2.4.2 Morphologies of PCFs

PMMA-*b*-PAN were electrospun into polymer fibers and carbonized. Regardless of the molecular weight, all block copolymer fibers were randomly aligned and showed similar packing structures (Figure S2.3). Heating the electrospun block copolymer fibers at 280 °C in air separated PMMA and PAN domains and developed sharp contrast on fiber surfaces (Figure S2.4), which was due to the partially cross-linked PAN and microphase-separation of PMMA-*b*-PAN.⁴⁵ The oxidized fibers were then subjected to pyrolysis at 800 °C, which fully decomposed PMMA and carbonized PAN to yield PCFs. The SEM images of various PCFs revealed that abundant mesopores were developed both on the fiber skins and in the cross sections (Figure 2.3). While increasing ϕ_{PAN} (from left to right in each row), the mesopores became smaller and less resolved on the carbon fiber skins. Overall, the mesopore size increased when the molecular weights of the PMMA block and the block copolymers increased.

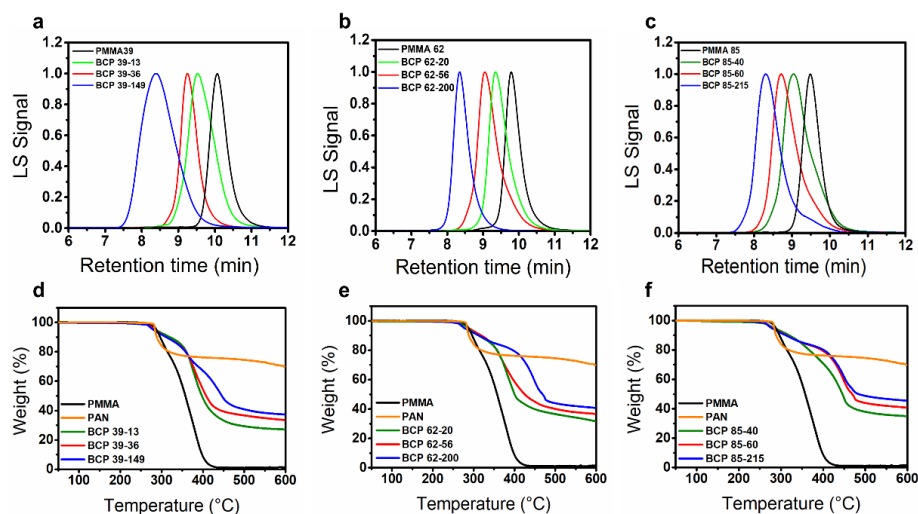


Figure 2.2. (a-c) SEC traces of PMMA and PMMA-*b*-PAN with various molecular weights: (a) PMMA 39 and BCP 39-X series, (b) PMMA 62 and BCP 62-X series, (c) PMMA 85 and BCP 85-X series. The profiles were collected by a light scattering detector and peak intensity was normalized for clarity. (d-f) TGA profiles of PMMA, PAN, and PMMA-*b*-PAN with various molecular weights and compositions: (d) PMMA 39, PAN, and BCP 39-X series, (e) PMMA 62, PAN, and BCP 62-X series, (f) PMMA 85, PAN, and BCP 85-X series.

Due to fast solvent vaporization during electrospinning and PAN crosslinking during thermal annealing at 280 °C in air,^{46,47} PMMA-*b*-PAN did not self-assemble into any thermodynamically equilibrated morphologies of a conventional diblock copolymer. Regardless of the molecular weight and composition, PMMA-*b*-PAN formed disordered and kinetically trapped nanostructures, which were pyrolyzed into disordered and interconnected porous carbons, similar to our previous reports.³⁹ Previously, small angle X-ray scattering (SAXS) was used to determine the pore size and spacing, but the SAXS showed broad scattering peaks and thus the d-spacing could not be accurately calculated.⁴⁸ The broad peaks were attributed to the crosslinking of PAN, which inhibited the formation of equilibrated structures of a classical diblock copolymer. Therefore in this work the pore sizes were characterized and analyzed by gas physisorption.

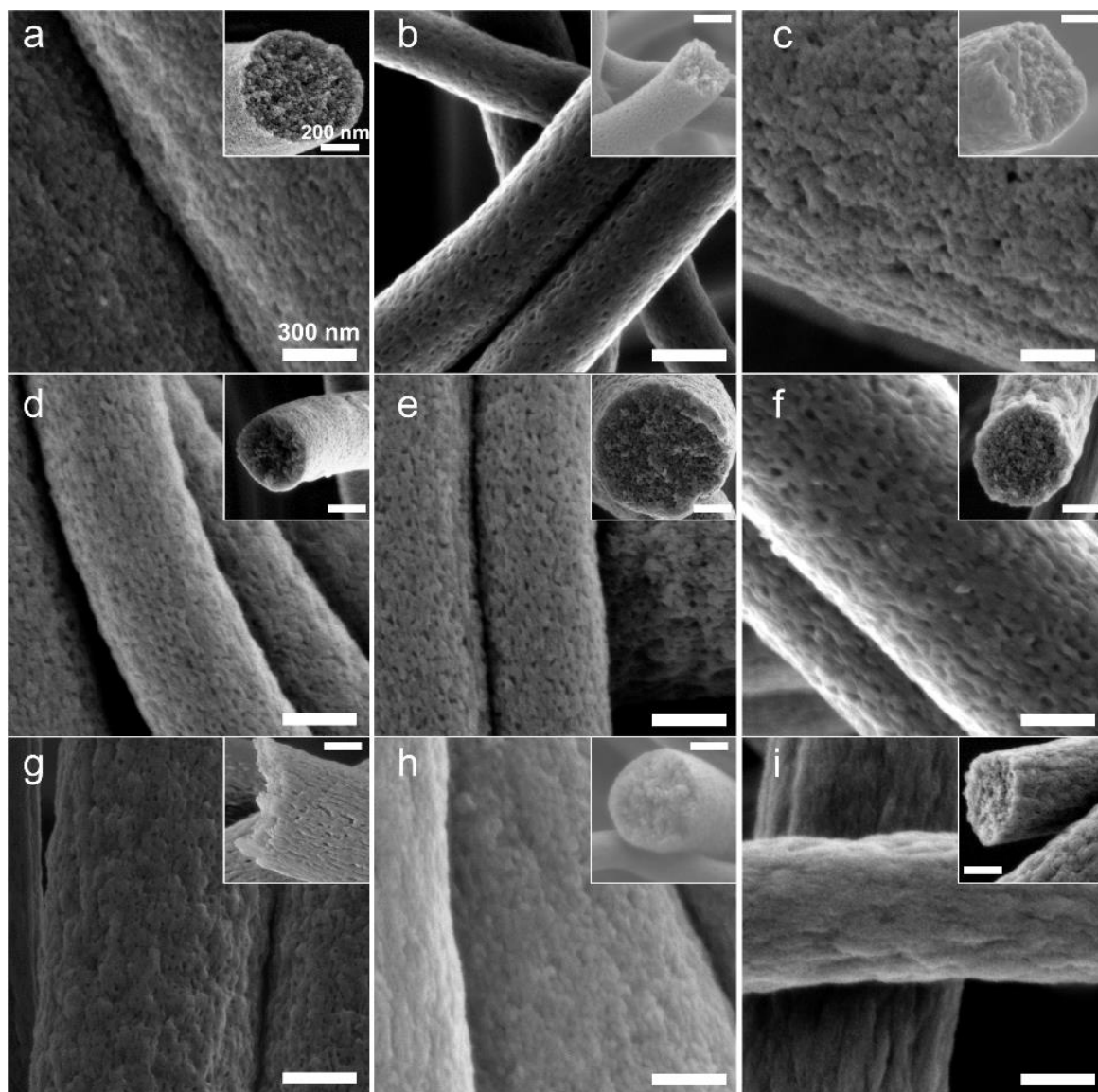


Figure 2.3. SEM images of PCFs, derived from various block copolymers (scale bars: 300 nm). (Inset) Cross-sectional SEM images of PCFs (scale bars: 200 nm). (a) PCF 39-13; (b) PCF 39-36; (c) PCF 39-149; (d) PCF 62-20; (e) PCF 62-56; (f) PCF 62-200; (g) PCF 85-40; (h) PCF 85-60; (i) PCF 85-215.

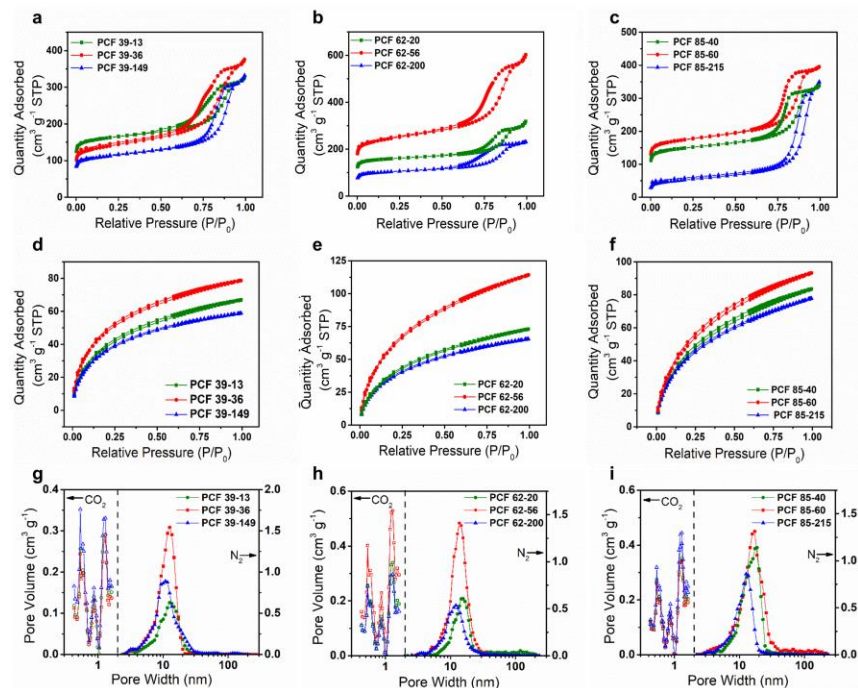


Figure 2.4. BET data of PCFs, (a-c) N_2 -physisorption isotherms, (d-f) CO_2 -physisorption isotherms, and (g-i) pore size distributions of various PCFs: (a, d, g) PCF 39-X series, (b, e, h) PCF 62-X series, and (c, f, i) PCF 85-X series.

Table 2.2. Physisorption data, ϕ_{PAN} , surface area, and mesopore peak sizes of various PCFs.

PCF	ϕ_{PAN}	Surface Area (N_2)	Surface Area (CO_2)	Mesopore Peak
		($m^2 g^{-1}$)	($m^2 g^{-1}$)	Size (nm)
PCF 39-13	0.25	421	119	12.7
PCF 39-36	0.47	615	123	11.7
PCF 39-149	0.79	228	124	10.9
PCF 62-20	0.24	605	126	15.7
PCF 62-56	0.47	918	208	13.7
PCF 62-200	0.79	391	118	12.1
PCF 85-40	0.31	562	132	18.6
PCF 85-60	0.41	657	129	17.2
PCF 85-215	0.71	342	141	13.7

2.4.3 BET surface areas and pore size distributions

The pore sizes and surface areas of PCFs were determined by gas physisorption. N₂ and CO₂ adsorption-desorption isotherms revealed type IV and I isotherms (Figure 2.4a-f), respectively, as defined by the International Union of Pure and Applied Chemistry (IUPAC).³⁶ The hysteresis of N₂ adsorption-desorption at $0.7 < P/P_0 < 0.9$ indicated the presence of mesopores (Figure 2.4a-c).⁴⁹ The maximum amount of N₂ adsorbed on the PCFs decreased in the sequence of $\phi_{\text{PAN}} \sim 0.50, 0.25$, and 0.75 (Figure 2.4a-c). N₂ derived surface areas were used to compare these PCFs to analogous carbon materials.^{50,51} Similarly, PCFs showed decreasing CO₂ adsorption in the sequence of $\phi_{\text{PAN}} \sim 0.5, 0.25$, and 0.75 (Figure 2.4d-f). CO₂-physisorption at 273 K probes micropores in porous materials⁵² and allows for implementation of NLDFT to calculate the micropore size distribution.^{53–55}

The micropore size distribution as determined from CO₂ adsorption exhibited multiple distinct peaks centered at $\sim 0.53, 0.86$, and 1.29 nm for all PCFs (Figure 2.4g-i). Differently, the mesopore distributions as determined from N₂ adsorption showed unimodal peaks owing to the well-controlled microphase-separation of PMMA-*b*-PAN (Figure 2.4g-i). The PMMA domains shrank during pyrolysis, thus leading to mesopores smaller than the block copolymer domains. The mesopore size was in the range of 10.9 to 18.6 nm (Figure 2.5a). The mesopore size strongly depended on the molecular weight and composition of block copolymers. In each series, the mesopore size decreased with an increasing ϕ_{PAN} . Although PMMA had the same molecular weight and thus supposedly similar domain size, the slightly smaller char yield of lower molecular weight PAN produced slightly less carbon and thus slightly larger mesopores than the BCPs with higher molecular-weight PAN. As expected, with the same ϕ_{PMMA} , the mesopore size increased when the BCP molecular weight was increased (Table 2.2).

The highest surface area of $918 \text{ m}^2 \text{ g}^{-1}$ was observed for PCF 62-56 derived from PMMA-*b*-PAN with a molecular weight of 62-*b*-56 kDa. Interestingly, in each BCP series, the highest surface areas of PCFs were all achieved by BCP with $\phi_{\text{PAN}} \sim 0.5$ (Figure 2.5b). This trend is associated with the volume ratio between PMMA and PAN. If PMMA is absent, the resulting fibers are mesopore-free, and therefore, they possess low surface areas ($\leq 200 \text{ m}^2 \text{ g}^{-1}$), as evidenced by previous reports.^{56,57} As PMMA is introduced into BCPs, mesopores are generated in PCFs and thus the surface area increases. The surface area continues to increase with increasing ϕ_{PMMA} , until it reaches a maximum at a critical ϕ_{PMMA} and the mesopores start to coalesce. Further increasing

ϕ_{PMMA} will decrease the surface area because an increasing number of pores are combined. When $\phi_{\text{PMMA}} = 1$, in principle, the surface area equals zero due to the little char yield of PMMA. In our case, the critical ϕ_{PMMA} was near 0.5, corresponding to a symmetric diblock copolymer. This is in agreement with our previous report³⁹ of PMMA-*b*-PAN with a molecular weight of 62-*b*-111 kDa ($\phi_{\text{PAN}} \sim 0.64$), which resulted in a surface area of 503 m² g⁻¹ slightly lower than the symmetrical block copolymer in this work.

Additionally, the molecular weight affected the pore size and surface area. On the one hand, as the molecular weight of PMMA was decreased, the small PMMA domains were packed increasingly densely and thus the surface area increased in the PCFs. On the other hand, the molecular weight of PAN also affected the degree of cross-linking and low-molecular-weight PAN yielded less carbon (Figure S2.5). Balancing the packing density of pores from PMMA and the cross-linking degree of PAN, the surface area initially increased and then decreased as the molecular weight of the block copolymer was decreased (Figure 2.5b).

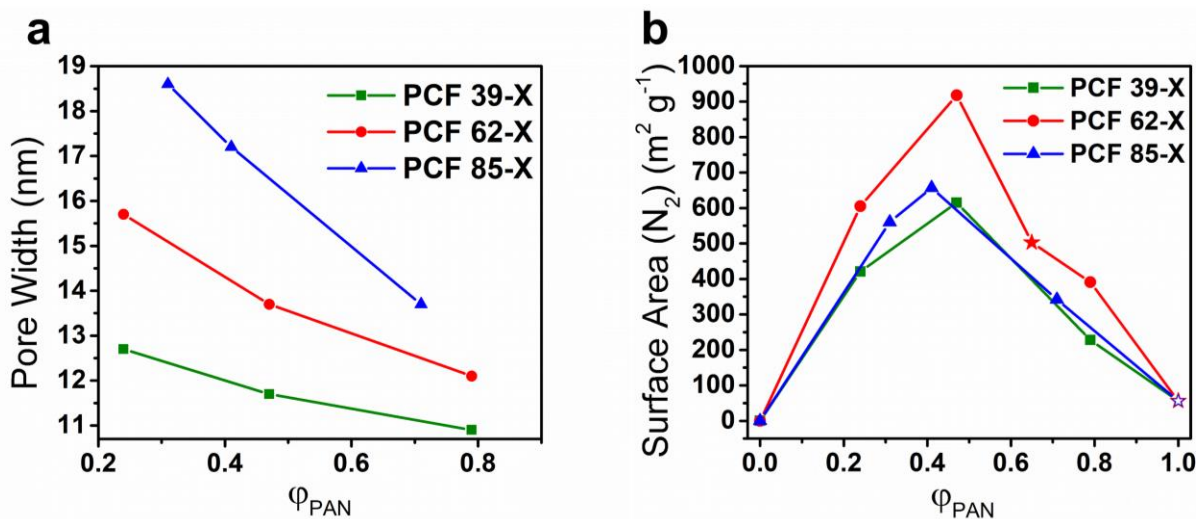


Figure 2.5. (a) Mesopore sizes and (b) surface area of all PCFs based on N₂ isotherms. Data points marked by filled and open stars are from ref³⁹ and ref⁶⁵ respectively.

2.4.4 Electrochemical properties

To understand how the structure affects the electrochemical properties of PCFs, we evaluated the ion-diffusion resistances *via* electrochemical impedance spectroscopy (EIS). The combined series resistance (R_s) and charge-transfer resistance (R_{ct}) were determined by fitting the Nyquist plots (Figure 2.6a-c) with an equivalent circuit model (Figure S2.1). The ion-diffusion resistance (R_d)

was obtained by linearly fitting the real part of impedance (Z') *versus* the inverse square root of frequency ($\omega^{-0.5}$) (Figure 2.6d-f). The R_s values of all PCFs were below $1.0\ \Omega$ (Figure 2.6a-c), which is typical for highly conductive carbons in concentrated electrolytes.⁵⁸ Notably, regardless of the molecular weight and composition, all PCFs exhibited similar degrees of graphitization, as quantified by the area ratio of G to D peaks ($I_G/I_D = 0.80 \pm 0.02$) in the Raman spectra (Table S2.2 and Figure S2.6). The similar degrees of graphitization were resulted from the identical pyrolysis conditions of the block copolymers. Due to the high degrees of graphitization, the carbon fibers were electrically conductive and showed low internal resistance. The electrical conductivity was confirmed by the series resistance of $R_s < 1\ \Omega$, as measured using EIS. The R_{ct} values were in the range of $0.43\text{--}0.71\ \Omega$ (Table S2.3). The diffusion resistance (σ) values correlated positively to ϕ_{PAN} . In other words, σ increased as ϕ_{PAN} was increased from 0.25 to 0.50, and to 0.75 in each BCP series (Figure S2.7). This phenomenon was attributed to pore width reduction as ϕ_{PAN} was increased (Figure 2.5a), which retarded ion diffusion. Similarly, at the same ϕ_{PAN} , an increasing molecular weight of PMMA in the BCP lowered σ of the PCF, due to the pore size widening that facilitated ion diffusion. For example, for BCPs with $\phi_{PAN} \sim 0.5$, when the M_n of PMMA was increased from 39 to 62, and to 85 kDa, the mesopore size of PCFs increased from 11.7 to 13.7, and to 17.2 nm. Consequently, the σ value of the PCFs decreased from 0.49 to 0.32, and to $0.28\ \Omega\ s^{-0.5}$ (Table S2.3). The diffusion resistance is a critical parameter that controls the rate capability of porous materials for energy storage.

2.4.5 Capacitance and rate capability

Cyclic voltammetry (CV) and chronopotentiometry (CP) were used to probe the gravimetric capacitances and rate capabilities of PCFs. All tests were conducted in a three-electrode configuration in 3 M aqueous KOH. KOH allowed for a wide potential window of $0.0\text{--}0.8\text{ V}$ vs. Ag/AgCl with high electrolyte and electrode stability.⁵⁹ Additionally, KOH served as a highly mobile electrolyte and ensured rapid infiltration of ions in the porous carbon fibers during charging-discharging.⁶⁰ All CV curves displayed no discernible redox peaks⁶¹ and maintained nearly rectangular shapes across the scan rates of $10\text{--}100\text{ mV s}^{-1}$ (Figures 2.7a-c and S8). The CP profiles (Figure 2.7d-f) showed no appreciable voltage plateaus. Both characteristics reflected that PCFs were excellent capacitive materials.³⁹

Capacitances calculated from the CV curves at 10 mV s^{-1} and the CP profiles at 10 A g^{-1} decreased in the following sequence: $\phi_{PAN} \sim 0.50$, 0.25, and 0.75 (Figure 2.7 and Table S2.4).

Comparison of the capacitance and the surface area showed a positive correlation (Figure S2.9). In each series, the PCFs derived from BCPs with $\phi_{\text{PAN}} \sim 0.50$ had the largest surface area (Figure 2.5b) and thus the highest capacitance (Figure 2.8). In addition to the surface area, the nitrogen and oxygen dopants also played an important role.⁶² Because the processing conditions were similar to our previous reports,^{39,48} the porous carbon fibers contained similar nitrogen and oxygen contents, which contributed to pseudocapacitance^{62–64} and showed excellent overall electrochemical performance. Among all PCFs, PCF 62-*b*-56 showed the highest capacitances of $345 \pm 10 \text{ F g}^{-1}$ at 10 mV s^{-1} and $218 \pm 9 \text{ F g}^{-1}$ at a current density of 10 A g^{-1} ($\pm$ values are standard deviations based on at least five devices).

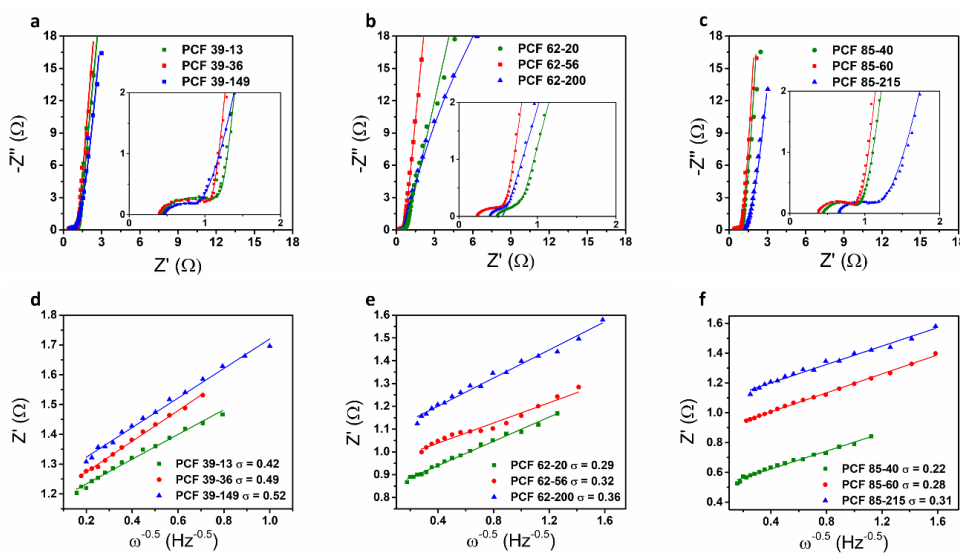


Figure 2.6. Nyquist and diffusion resistance, (a-c) Nyquist plots and (d-f) Z' vs. $\omega^{-0.5}$ plots of PCFs: (a and d) PCF 39-X series, (b and e) PCF 62-X series, and (c and f) PCF 85-X series. The solid lines in d, e, and f are best fitting lines. The slopes represent the diffusion resistances (σ) in $\Omega \text{ s}^{0.5}$.

In all three series, PCFs derived from BCPs with $\phi_{\text{PAN}} \sim 0.25$ retained the most capacitance when the scan rate was increased from 10 to 1000 mV s^{-1} , followed by PCFs derived from BCPs with $\phi_{\text{PAN}} \sim 0.50$ and then $\phi_{\text{PAN}} \sim 0.75$ (Figure 2.7g-i). The trends in rate capabilities are correlated to the porous structures. At slow scan rates (*e.g.*, 10 mV s^{-1}), ions have sufficient time to reach all the ion-accessible surfaces of the electrodes, and therefore the surface area is the major factor determining the capacitances. The loss in capacitance at elevated scan rates is mainly due to the inadequate rates of ion diffusion that reduce the effective ion-accessible surface area. Based on

N₂- and CO₂-sorption, the change in the micropore volume was insignificant among all the PCFs, but the change in the mesopore volume was drastic as M_n and ϕ_{PAN} varied (Figure S2.10). Hence, the effect of micropores on the electrochemical performance was minor compared to that of the mesopores. Therefore, in each series, PCFs with the largest mesopores (Figure 2.5a) and the smallest σ (Figure S2.7) exhibit the best rate capability (Figure 2.7g-i).

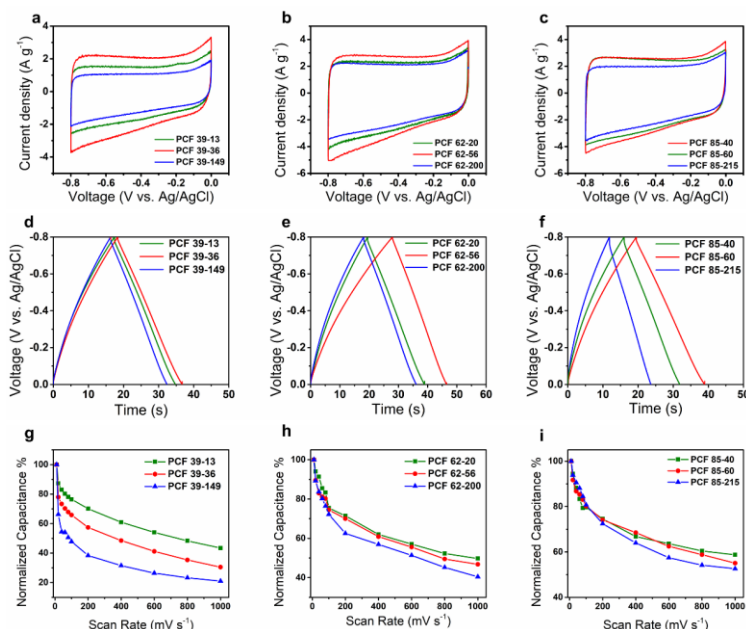


Figure 2.7. (a-c) CV curves at 10 mV s⁻¹, (d-f) CP profiles at 10 A g⁻¹, and (g-i) capacitance retentions at scan rates from 10 to 1000 mV s⁻¹ of different PCFs: (a, d, g) PCF 39-X series, (b, e, h) PCF 62-X series, and (c, f, i) PCF 85-X series. The capacitance retentions were normalized to the capacitances at 10 mV s⁻¹ for each PCF.

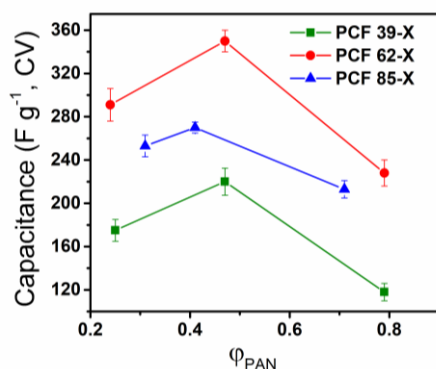


Figure 2.8. The average gravimetric capacitances of PCFs at 10 mV s⁻¹ in 3 M KOH. The error bars are standard deviations based on the capacitances of at least five electrodes.

2.5 Conclusions

In this chapter we describe a systematic study that designs block copolymers of appropriate molecular weights and compositions to obtain porous carbon fibers with optimal structures and electrochemical performances for capacitive energy storage. Regardless of the composition, PMMA-*b*-PAN did not form any spherical, cylindrical, and lamellar structures. Instead, PMMA-*b*-PAN formed disordered and kinetically trapped nanostructures after electrospinning and thermal treatment. The thermal treatment cross-linked PAN and impeded the self-assembly of PMMA-*b*-PAN into any classical block copolymer morphology. The resultant PCFs inherited the disordered block copolymer nanostructures and exhibited disordered mesopores after pyrolysis. The mesopore size in the PCFs ranged from 10.9 to 18.6 nm, depending on the molecular weight of the sacrificial PMMA block, as well as the volume fraction of the PAN block. The surface area and gravimetric capacitance peaked at symmetric diblock copolymers, that is, the molecular weights of PMMA and PAN were comparable. PMMA-*b*-PAN of an intermediate molecular weight showed a higher surface area and capacitance than those of lower or higher molecular weights. Particularly, the PCFs derived from PMMA-*b*-PAN with a molecular weight of 62-*b*-56 kDa achieved the highest surface area of 918 m² g⁻¹ and the largest gravimetric capacitances of 345±10 F g⁻¹ at 10 mV s⁻¹. Moreover, an increase in mesopore width revealed a decreasing ion diffusion resistance from 0.52 to 0.22 Ω s^{-0.5}, which was correlated to an improved rate capability.

This work provides a rational design of PMMA-*b*-PAN block copolymer precursors for creating porous carbon fibers with controlled porous structures, surface areas, and electrochemical properties. We have elucidated the interplays among block copolymer molecular weights, PCF nanostructures, and electrochemical properties. The findings not only highlight the tunability of the structure-property-performance of PCFs, but also provide guidelines for designing block copolymers to create porous carbon fibers for diverse applications ranging from electrochemical energy storage to water purification, and to heterogeneous catalysis.

2.6 Supporting Information

Scheme S2.1. RAFT polymerization of PMMA-*b*-PAN. CDB, cumyl dibenzothioate; AIBN, azobisisobutyronitrile; AN, acrylonitrile; and DMSO, dimethyl sulfoxide.

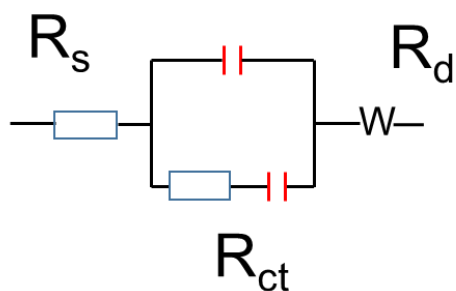
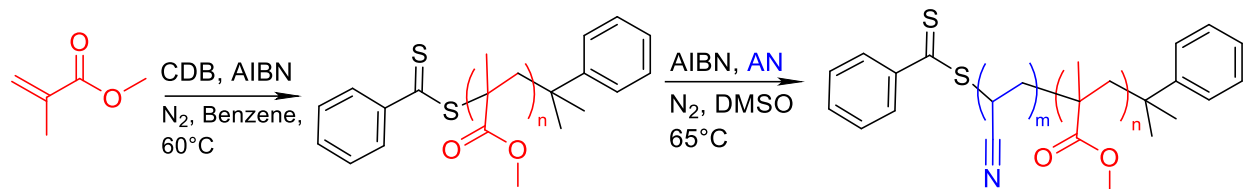


Figure S2.1. An equivalent circuit model for fitting the Nyquist plots. R_s is diffusion resistance; R_{ct} is charge-transfer resistance; and R_d is diffusion resistance.

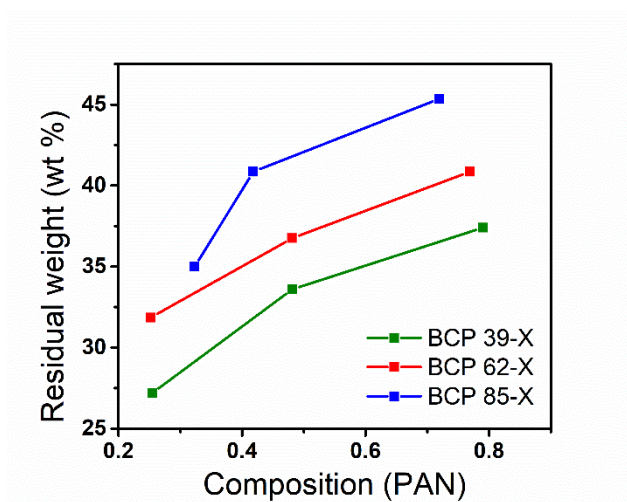


Figure S2.2. Char yields of PMMA-*b*-PAN block copolymers after heating of 600 °C in N_2 .

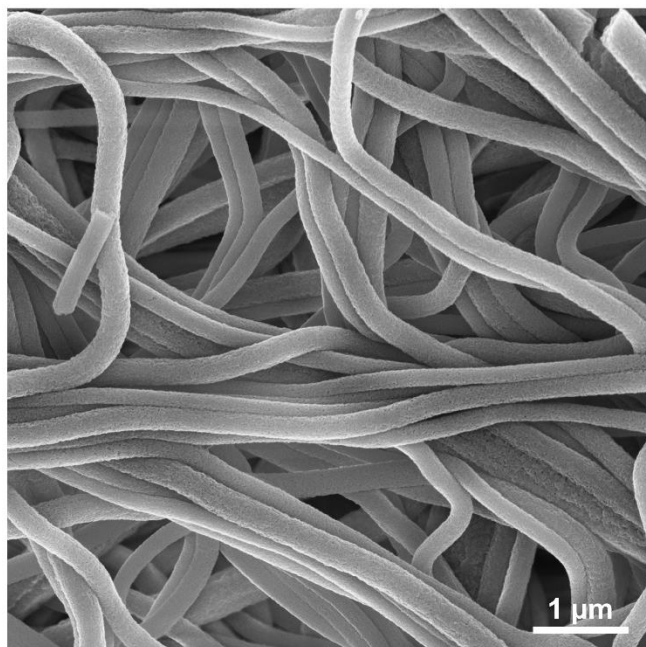


Figure S2.3. A representative SEM image of PCF 62-56 after pyrolysis at 800 °C under a nitrogen atmosphere.

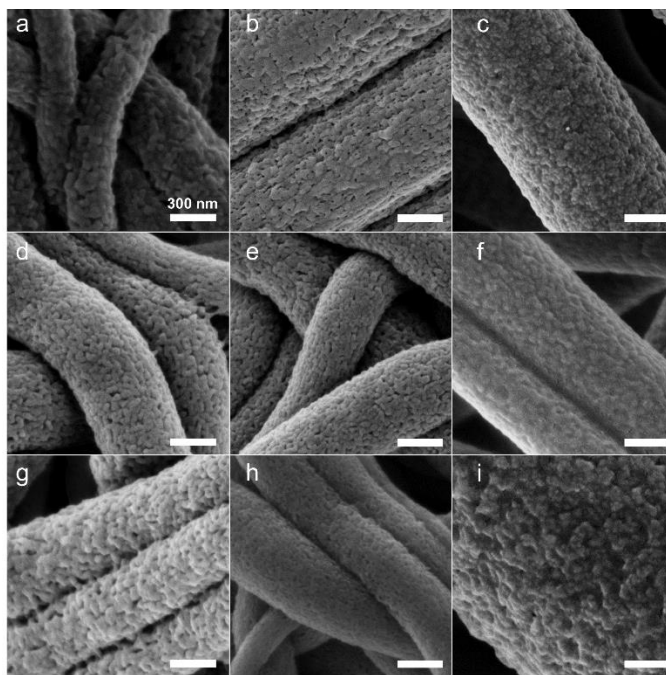


Figure S2.4. SEM images of block copolymer fibers after oxidation at 280 °C in air: (a) BCP 39-13; (b) BCP 39-36; (c) BCP 39-149; (d) BCP 62-20; (e) BCP 62-56; (f) BCP 62-200; (g) BCP 85-40; (h) BCP 85-60; (i) BCP 85-215. Scale bars: 300 nm.

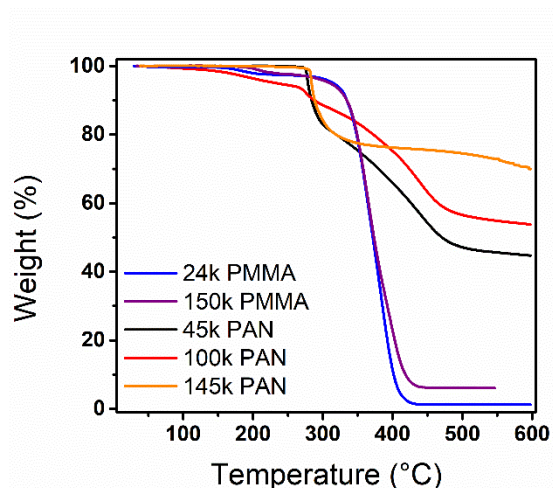


Figure S2.5. Representative TGA traces of PMMA and PAN with various molecular weights in Daltons.

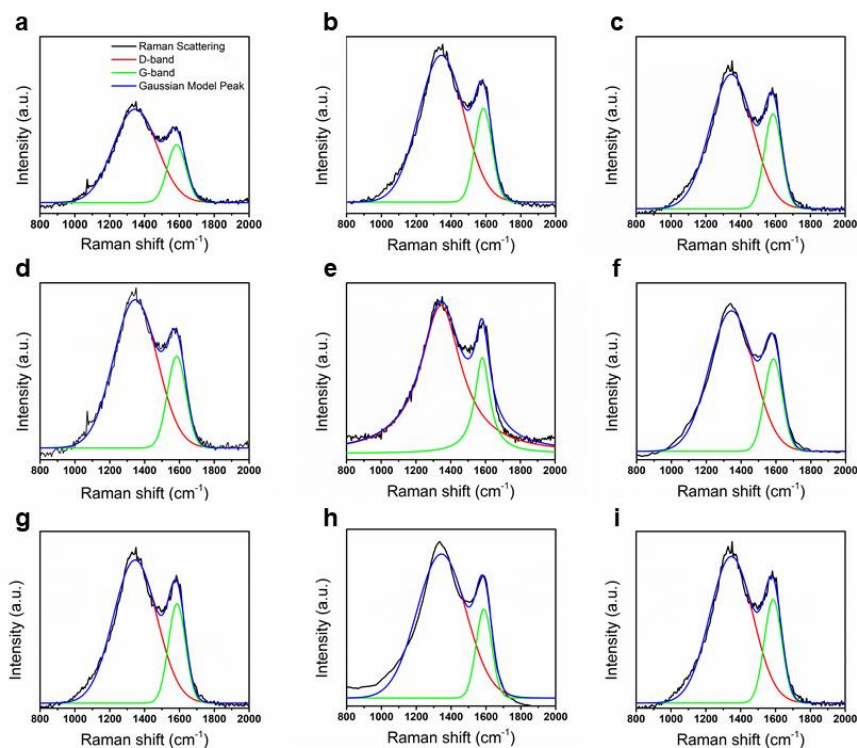


Figure S2.6. Raman spectra of PCFs: (a) PCF 39-13, (b) PCF 39-36, (c) PCF 39-149, (d) PCF 62-20, (e) PCF 62-56, (f) PCF 62-200, (g) PCF 85-40, (h) PCF 85-60, (i) PCF 85-215. The black curves are experimental data. The red, green, and blue solid lines are the deconvoluted D band, G band, and the fitting, respectively.

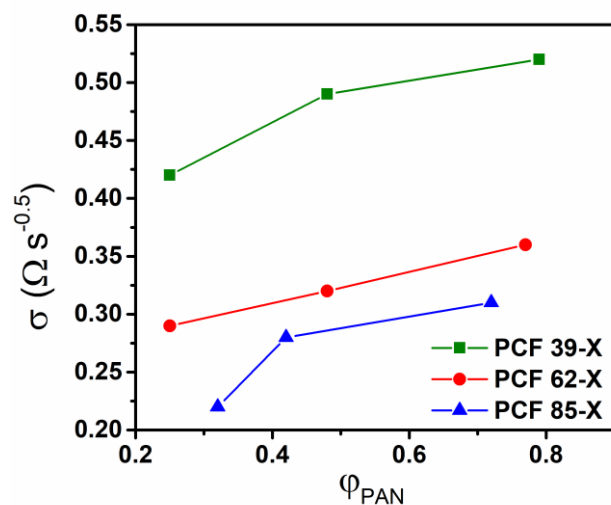


Figure S2.7. Ion-diffusion resistances (σ) of all PCFs.

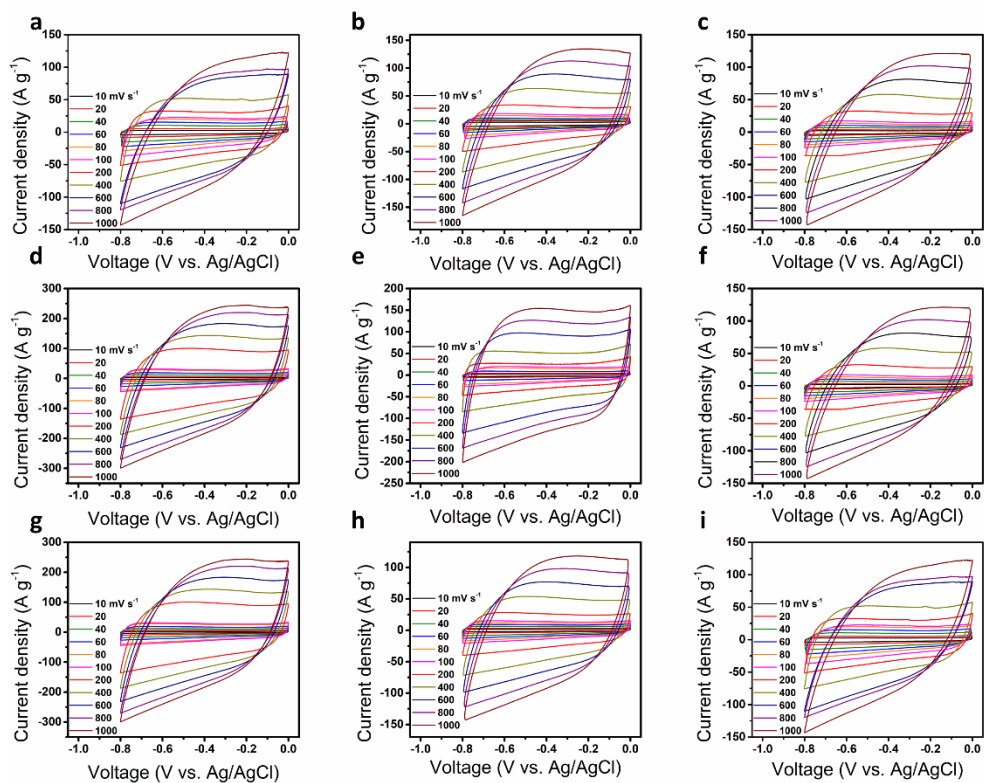


Figure S2.8. Cyclic voltammograms of a) PCF 39-13, b) PCF 39-36, c) PCF 39-149, d) PCF 62-20, e) PCF 62-56, f) PCF 62-200, g) PCF 85-40, h) PCF 85-60, and i) PCF 85-215 at scan rates from 10 to 1000 mV s^{-1} .

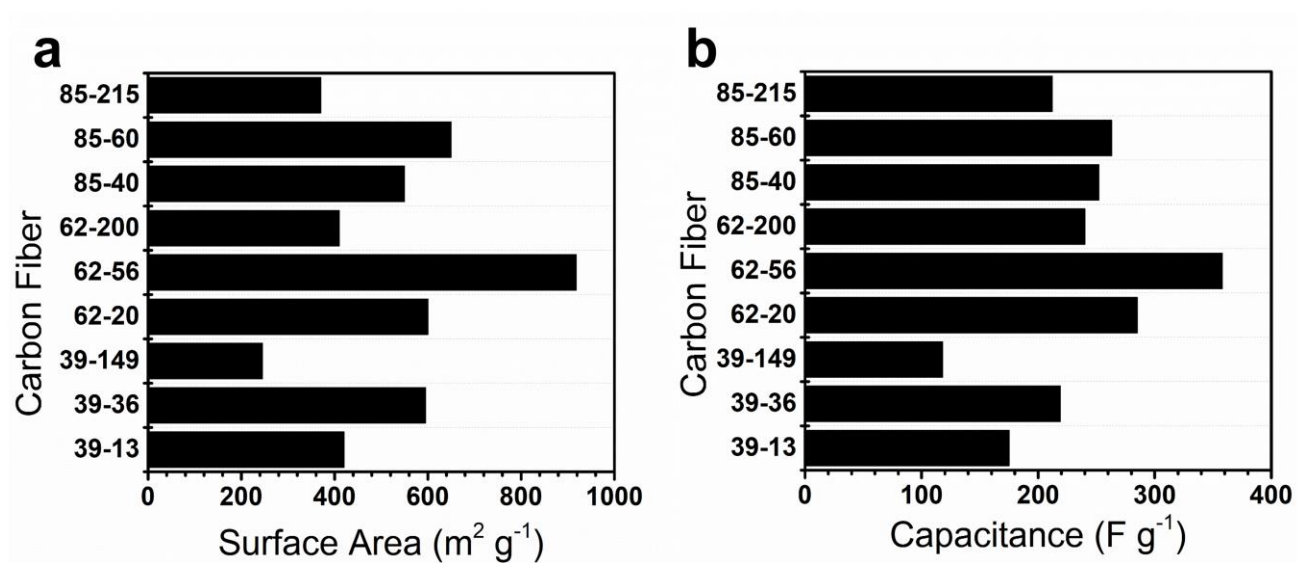


Figure S2.9. Correlation of the (a) BET surface areas and (b) maximal gravimetric capacitances of PCFs.

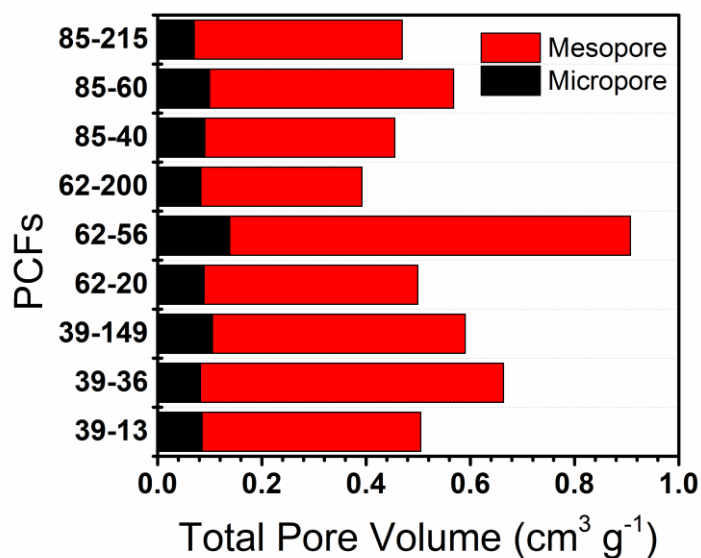


Figure S2.10. Volumes of mesopores (black) and micropores (red) in PCFs, as measured by N_2 and CO_2 isotherms, respectively.

Table S2.1. Char yields of PMMA, PAN, and PMMA-*b*-PAN at 600 °C in N₂, as determined by TGA.

Designation	ϕ_{PAN}	Char yield (%)
PAN	1.00	69
PMMA 39	-	0
BCP 39-13	0.25	27
BCP 39-36	0.48	33
BCP 39-149	0.79	37
PMMA 62	-	0
BCP 62-20	0.25	31
BCP 62-56	0.48	36
BCP 62-200	0.77	40
PMMA 85	-	0
BCP 85-40	0.32	35
BCP 85-60	0.42	40
BCP 85-215	0.72	45

Table S2.2. I_G/I_D peak ratio of PCFs based on Gaussian deconvolution of the Raman spectra.

	PCF	PCF	PCF	PCF	PCF	PCF	PCF	PCF	PCF
	39-13	39-36	39-149	62-20	62-56	62-200	85-40	85-60	85-215
I_G/I_D	0.78	0.82	0.78	0.81	0.80	0.81	0.82	0.81	0.82

Table S2.3. Total series resistance (R_s), charge transfer resistance (R_{ct}), and diffusion resistance (R_d) of PCFs based on electrochemical impedance spectroscopy with a three-electrode configuration.

PCF	R_s (Ω)	R_{ct} (Ω)	R_d (Ω s ⁻¹)
PCF 39-13	0.46	0.40	0.77
PCF 39-36	0.38	0.69	0.74
PCF 39-149	0.47	0.57	0.55
PCF 62-20	0.23	0.35	0.50
PCF 62-56	0.56	0.41	0.32
PCF 62-200	0.38	0.50	0.55
PCF 85-40	0.44	0.47	0.31
PCF 85-60	0.36	0.55	0.28
PCF 85-215	0.63	0.73	0.30

Table S2.4. Specific capacitances (C_{sp}) of PCFs at various scan rates as determined by cyclic voltammetry (CV) in a three-electrode configuration.

PCF	C_{sp} (10 mV s ⁻¹) (F g ⁻¹)	C_{sp} (100 mV s ⁻¹) (F g ⁻¹)
PCF 39-13	175	134
PCF 39-36	220	145
PCF 39-149	118	77
PCF 62-20	291	220
PCF 62-56	350	261
PCF 62-200	224	161
PCF 85-40	253	199
PCF 85-60	270	215
PCF 85-215	213	172

2.7 Acknowledgments

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Chapter 3. Capacitive Organic Dye Removal by Block Copolymer Based Porous Carbon Fibers

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3.1 Abstract

Block copolymer based porous carbon fibers (PCF) have hierarchical pores, high surface areas, and excellent electrical/ion conductivities. Herein PCF has been synthesized from poly(methyl methacrylate)-*block*-poly(acrylonitrile) and utilized for organic dye removal. The PCF contained hierarchical macro, meso, and micropores with a surface area of $780 \text{ m}^2 \text{ g}^{-1}$. The electrosorptive behavior of PCF was well described by the Langmuir isotherm and the Weber-Morris model. Based on the model, the interconnected hierarchical pores contributed to easy accessibility of dye ions to the inner surface sites within PCF, resulting in a high electrosorption capacity of 1360 mg g^{-1} , reaching $\sim 87\%$ of the theoretical maximum. The PCF showed a capacity loss of $<0.5\%$ over 10 cycles during a 240-h operation period. Thanks to the hierarchical pores that allowed for rapid ion desorption, the PCF could be easily regenerated. Lastly, depending on the electrode configuration, the PCF could selectively remove anionic dye, cationic dye, or both. The findings herein provide a fundamental understanding of electrosorptive behavior of block copolymer-based porous carbon fibers, enabling future development in filtration applications.

3.2 Introduction

Wastewater from paint, textile, plastic, paper, and cosmetic industries^{1–4} often contains high concentrations of organic dyes and is a major environmental effluent.⁵ Toxicity investigations have shown deleterious impacts of organic dyes on ecosystems and human health.^{6,7} Particularly, organic dyes constituting anionic and cationic species have mutagenic and carcinogenic effects even at low concentrations,⁸ often leading to dysfunctional physiological systems in humans and

other animals.^{9–11} Dreadfully, the degradation resistance of these organic dyes poses a serious and lasting threat to the environment.¹²

Over the years a number of methods have been developed to treat organic dye-containing wastewater. The methods include coagulation,¹³ physisorption,¹⁴ photocatalysis,¹⁵ and electrocatalysis.¹⁶ The high cost, low regeneration capacity, and slow processing of these methods, however, disfavor their wide use in wastewater treatment.^{1,17} For example, coagulation is reliable for dye entrapment but often produces sludge residue as secondary waste.^{18–20} Physisorption is a rapid process but the reusability/regeneration of absorbents remains challenging.²¹ In contrast, electrosorption, which is based on electrical double layers, has garnered interest owing to its low-cost, reusability, high stability, and non-production of secondary waste.^{22–24} For this purpose, carbon serves as a low cost material suitable for electrosorption thanks to its electrical conductivity, high surface area, and high capacity.²⁵

Activated carbon is a typical material for electrosorption, but its performance has been limited by sluggish ion infiltration and lack of effective surface area.²⁶ Means for improvement includes increasing surface area and pore volume, introducing novel surface functionalities, and adjusting the porous structures.^{27–29} Many excellent improvements have been implemented on a variety of carbon materials including carbon nanotubes,³⁰ carbon aerogels,³¹ and carbon composites.³² It is known that parameters such as morphology, surface area, and pore size control of carbon materials are all imperative for the capability of electrosorbing charged pollutants in wastewater.^{33–36} For example, carbon nanotubes, graphene, and carbon fibers show higher-than-average electrosorption capabilities per Brunauer-Emmett-Teller (BET) based surface area.^{37,38} Pore abundance and size affects the surface area and adsorption rate.^{39,40} Notably hierarchal pores improve adsorption capacity, rate, and reusability.⁴¹ Thus, utilization of a carbon material, which has a tunable pore size, high surface area, controllable morphology, and hierarchical porosity, will be vital for high-performance organic dye removal from wastewater, as well as for mechanistic investigation of electrosorption behaviors.

Herein, we employ our recently developed hierarchical porous carbon fibers (PCF)^{42–45} with controlled porosity from block copolymers in electrosorptive wastewater treatment. The uniform mesopores, continuous carbon fiber matrices, and high surface areas of PCF offer high adsorption capacity and fast infiltration rates for both cationic and anionic dyes. The PCF demonstrated a high capacity for dye adsorption (1360 mg g⁻¹ - the weight of the adsorbed dye was more than that of

the active material, PCF) with excellent reusability, showing <0.5% loss of dye-adsorption capacity over 10 cycles and a duration of 240 h. Furthermore, the PCF could adsorb multiple dyes or selectively adsorb one type of the dye. Lastly, kinetic and adsorption isotherm models elucidate the mechanism of electrosorption within the hierarchical PCF.

3.3 Experimental Section

3.3.1 Materials

Methyl methacrylate (MMA, $\geq 99\%$), acrylonitrile (AN, $\geq 99\%$), 2,2'-azobis(2-methylpropionitrile) (AIBN $\geq 98\%$), benzene ($\geq 99\%$), aluminum oxide (activated, neutral, Brockmann Activity I), *N,N*-dimethylformamide (DMF, $\geq 99.7\%$), and dimethyl sulfoxide (DMSO, $\geq 99.9\%$) were purchased from Sigma-Aldrich. Cumyl dithiobenzoate (CDB) was synthesized *via* a previously reported protocol.^{42,43,45,46} Methyl orange (MO) and methylene blue (MB) dyes were purchased from VWR and Merck, respectively. Methanol was used for polymer precipitation. Nickel foam (MTI Corporation) was used as electrode substrates. MMA and AN were purified by passing through an alumina column; all other chemicals were used as received.

3.3.2 Preparation of PCFs

Poly(methyl methacrylate)-*block*-poly(acrylonitrile) (PMMA-*b*-PAN) was synthesized *via* reversible addition-fragmentation chain transfer (RAFT) polymerization modified from a previous report.⁴³⁻⁴⁵ First, MMA (35.0 mL, 309 mmol), CDB (84.3 mg, 0.309 mmol), and AIBN (25.4 mg, 0.155 mmol) were dissolved in benzene (51.6 mL) in a 100-mL Schlenk flask. The mixture was subjected to three cycles of freeze-pump-thaw (FPT) followed by back-filling with N₂ to remove dissolved oxygen. The reaction proceeded at 60 °C for 24 h resulting in a PMMA macro-chain transfer agent (macro-CTA). The macro-CTA was precipitated in methanol, filtered, and dried under vacuum for 12 h. The purified macro-CTA (0.650 g, 10.8 μ mol) was then mixed with AN (2.60 mL, 43.3 mmol), AIBN (0.44 mg, 2.7 μ mol), and DMSO (7.22 mL) to synthesize PMMA-*b*-PAN. The mixture was degassed by three FPT cycles and then heated in an oil bath at 65 °C under an N₂ atmosphere for 18 h. The resultant PMMA-*b*-PAN was purified following the same steps as those of PMMA macro-CTA. The number average molecular weights (M_n) and

polydispersity index (PDI) were measured with size exclusion chromatography (SEC) (EcoSEC HLC-8320GPC) equipped with a light scattering detector (DynaPro Nanostar photometer).

PMMA-*b*-PAN ($M_n = 62\text{-}b\text{-}79$ kDa, PDI = 1.10) was dissolved in DMF at a concentration of 18 wt.% overnight. The dissolved PMMA-*b*-PAN was electrospun at a flow rate of 0.020 mL min^{-1} and a voltage bias of 18 kV provided by a high-voltage supply (Model P030HP1, Acopian Technical Company). Electrospun fibers were collected by an aluminum drum with a rotating speed of ~ 120 rpm. The as-spun fibers were oxidized and stabilized at $280\text{ }^{\circ}\text{C}$ for 8 h in air and then pyrolyzed at $800\text{ }^{\circ}\text{C}$ for 1 h in an electrical tube furnace (Model STF55433C-1, Lindberg/Blue M) under one atmosphere of N_2 with a constant flow rate of 200 standard cubic centimeters per minute. The resultant PCF was used without further activation.

3.3.3 Fabrication of electrosorption electrodes.

PCF ($\sim 3\text{-}4$ mg) was sandwiched between two pieces of nickel foam ($\sim 3.5 \times 6\text{ cm}^2$) and pressed at 4 metric tons using a benchtop hydraulic shop press (Stongway, Model 46269). The actual mass loading of PCF was determined using an analytical balance (Model Mettler Toledo XSE105) with a sensitivity of ± 0.01 mg. The mass was checked before and after pressing to account for any material loss during the pressing process. The electrodes were placed in a home-made electrosorption cell for tests.

3.3.4 Material characterization

Thermal gravimetric analysis (TGA) (Discovery TGA5500, TA Instruments) was performed under an N_2 flow of 25 mL min^{-1} at a temperature-ramp rate of $10\text{ }^{\circ}\text{C min}^{-1}$ from 25 to $600\text{ }^{\circ}\text{C}$. The carbonized fibers were imaged with a scanning electron microscope (LEO Zeiss 1550 SEM, acceleration voltage = 2 kV, working distance ~ 2 mm). N_2 and CO_2 physisorption was conducted at 77 K and 273 K, respectively, on a 3Flex Pore Analyzer (Micrometric Instruments Company). Prior to physisorption, PCF was degassed at $90\text{ }^{\circ}\text{C}$ for 1 h and $300\text{ }^{\circ}\text{C}$ for 10 h to remove any potential adsorbents on the carbon surface. Surface areas were calculated based on Brunauer-Emmett-Teller (BET) theory. Pore size distributions were obtained using non-local density functional theory (NLDFT), similar to a previous report.⁴⁷ Ultraviolet-visible (UV-vis) spectra were acquired using an Agilent Cary 5000 UV-vis-NIR spectrophotometer. All electrochemical

tests were carried out using an electrochemical workstation (PARSTATS 4000+, Princeton Applied Research, Ametek Inc.)

3.3.5 Capacitive filtration

A custom-built capacitive filtration cell with an injection port and extraction port was filled with 15 mL of dye-containing solution. The dye concentration ranged from 6.25 to 1000 mg L⁻¹. NaCl (supporting electrolyte) was added to all dye solutions before electrosorption to reach a final concentration of 100 mg L⁻¹. To remove the dyes using PCF, a direct voltage bias of 0.8 V was applied to two symmetrical electrodes immersed in the solution. The electrosorption of dyes by PCF was conducted at room temperature without convection. To regenerate the PCF, the electrodes were placed in deionized water. The electrodes were allowed to equilibrate for 1 h at room temperature by applying a bias of 0 V using an external source. This process allowed for the desorption of dye ions on the surface of the PCF.

3.3.6 Data analysis

MO dye was used for analyzing the electrosorption kinetics and isotherms. The MO dye concentration was calculated from the maximum absorbance wavelength (λ) at 463 nm. Given an initial dye concentration in solution C_o (mg L⁻¹), the dye removal percentage was calculated according to

$$\text{removal\%} = \frac{C_o - C_e}{C_o} \times 100\% \quad (3.1)$$

where C_e (mg L⁻¹) was the equilibrium concentration of the dye in solution after electrosorption. Thus, the remaining percentage of dye in solution (remaining dye%) was calculated according to

$$\text{remaining dye\%} = 100\% - \text{removal\%} \quad (3.2)$$

The loading of electrosorbed dye on PCF (q_t , mg g⁻¹) was calculated by

$$q_t = \frac{(C_o - C_e)V}{M} \quad (3.3)$$

where V (L) was the volume of the solution and M (g) was the mass of the active material (PCF). To further investigate the adsorption mechanism, pseudo-first order, pseudo-second order, and Weber-Morris (intra-particle) kinetic models were applied to fit the electrosorption data. The pseudo-first order equation used was:⁴⁸

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (3.4)$$

where q_e (mg g⁻¹) and q_t (mg g⁻¹) were the loading of dye on PCF at equilibrium and at time t , respectively; k_1 was the rate constant (min⁻¹). By applying the boundary conditions of $q_t = 0$ at $t = 0$ and $q_t = q_e$ at equilibrium equation (3.4) was converted to:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (3.5)$$

The pseudo-second order kinetic model was calculated with the following equation:⁴⁸

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (3.6)$$

Applying the boundary conditions of $q_t = 0$ at $t = 0$ and $q_t = q_e$ equilibrium converted equation (3.6) to:

$$\frac{t}{q_t} = \left(\frac{1}{k_2 q_e^2} \right) + \frac{t}{q_e} \quad (3.7)$$

Linear fitting of t/q_t vs. t afforded k_2 from the slope if the pseudo-second order model was valid.

The intra-particle mass transfer diffusion model (Weber-Morris model)⁴⁹ was applied through the equation:

$$q_t = k_i t^{0.5} + B \quad (3.8)$$

where k_i was the intra-particle diffusion rate constant (mg g⁻¹ min^{-1/2}) for adsorption, and B (mg g⁻¹) was the intercept.

To study the interaction between PCF and dye ions, the Freundlich and Langmuir isotherms were applied to the electrosorption data. The Freundlich isotherm was described as follows:

$$q_e = K_f C_0^{b_f} \quad (3.9)$$

which was re-written in a linear form of:

$$\ln q_e = \ln K_f + b_f \ln C_0 \quad (3.10)$$

where K_f was the Freundlich constant and b_f was the adsorption intensity constant.

The Langmuir isotherm model assumes that adsorption sites are homogeneous on the active material, in other words, there are no adsorbate-adsorbate interactions. The equation for the Langmuir isotherms was written as:

$$q_e = \frac{q_{e,max} K_L C_0}{1 + K_L C_0} \quad (3.11)$$

and the linear Langmuir model form was:

$$\frac{1}{q_e} = \frac{1}{q_{e,max} K_L} \left(\frac{1}{C_0} \right) + \frac{1}{q_{e,max}} \quad (3.12)$$

where K_L (L mg⁻¹) was the Langmuir constant and $q_{e,max}$ (mg g⁻¹) was the theoretical maximum dye loading. Additionally, the separation factor or equilibrium factor, R_L , as defined by the Langmuir model was evaluated by the following relation:

$$R_L = \frac{1}{1 + K_L C_o} \quad (3.13)$$

3.4 Results and Discussion

3.4.1 Characterization of the block copolymer

The carbon fiber precursor PMMA-*b*-PAN was synthesized *via* RAFT polymerization and had a number average molecular weight (M_n) of 62-*b*-79 kDa and a PAN volume fraction (ϕ_{PAN}) of 0.56, as determined by SEC (**Figure 3.1a**).⁵⁰ The ϕ_{PAN} was further confirmed by TGA based on char yield (**Figure 3.1b**). PMMA was fully decomposed with zero char yield and PAN served as the source of carbon with a char yield of 72% at 600 °C.⁵¹ In the TGA traces of PMMA-*b*-PAN, the weight loss between 270 and 325 °C was attributed to partial oxidation of PAN and formation of carbon monoxide, carbon dioxide, hydrogen cyanide, and other products,⁵² similar to the first weight loss of PAN homopolymer. Typically, PAN crosslinked intramolecularly^{53,54} below 290 °C and intermolecularly⁵⁵ above 290 °C. At ~350 °C, the PMMA block in PMMA-*b*-PAN decomposed rapidly, similar to the PMMA homopolymer. Above 500 °C, the cross-linked PAN was pyrolyzed into a carbon matrix. The block copolymer showed an overall char yield of 39% at 600 °C attributed to the pyrolysis of PAN. This char yield corresponded to $\phi_{PAN} \sim 0.55$ in agreement with that determined from SEC. We chose this ϕ_{PAN} based on our previous report,⁵⁰ where PMMA-*b*-PAN with $\phi_{PAN} \sim 0.5$ produced porous carbon fibers with hierarchical, interconnected pores of a high surface area and pore volume.

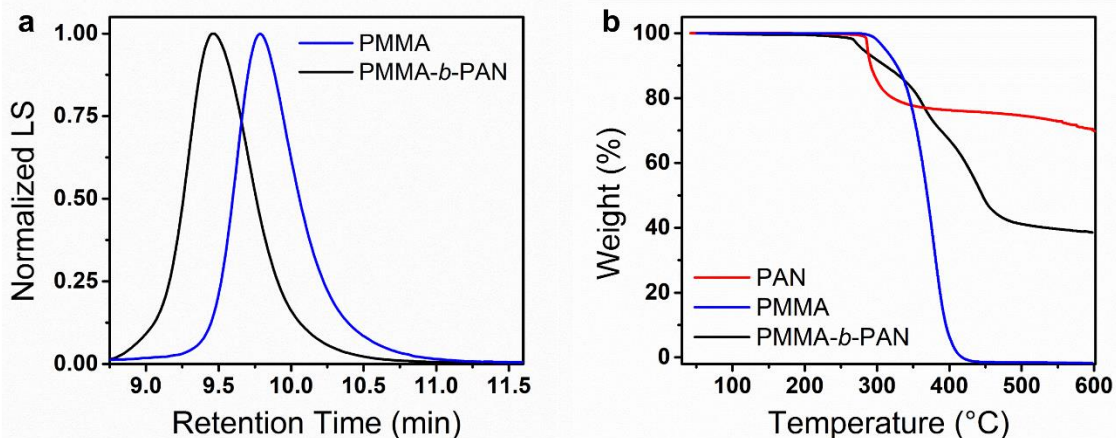


Figure 3.1. Polymer characterization. (a) SEC traces of PMMA macro-CTA and PMMA-*b*-PAN using a light-scattering (LS) detector. The peak intensities were normalized to show the changes in retention time after copolymerization. (b) TGA traces of PAN, PMMA, and PMMA-*b*-PAN.

3.4.2 Characterization of porous carbon fibers

The as-synthesized PMMA-*b*-PAN was electrospun into a mat of randomly oriented polymer fibers with inter-fiber distances of $<1\ \mu\text{m}$ (**Figure 3.2a**). After pyrolysis, the complete decomposition of PMMA resulted in uniform mesopores in the fibers, whereas the cross-linked PAN was converted into a continuous fibrous carbon matrix (**Figure 3.2b,c**). N_2 and CO_2 physisorption assessed the porosity and surface area in the ranges of mesopores and micropores, respectively (**Figure 3.2d,e**).⁵⁶ Specifically, N_2 -physisorption showed a high surface area of $780\ \text{m}^2\ \text{g}^{-1}$. Based on non-local density functional theory (NLDFT),^{43–45} the pore size distribution showed multiple peaks at ~ 0.53 , 0.86 , and $1.30\ \text{nm}$ in the micropore range and a unimodal peak at $13\ \text{nm}$ in the mesopore range (**Figure 3.2f**).

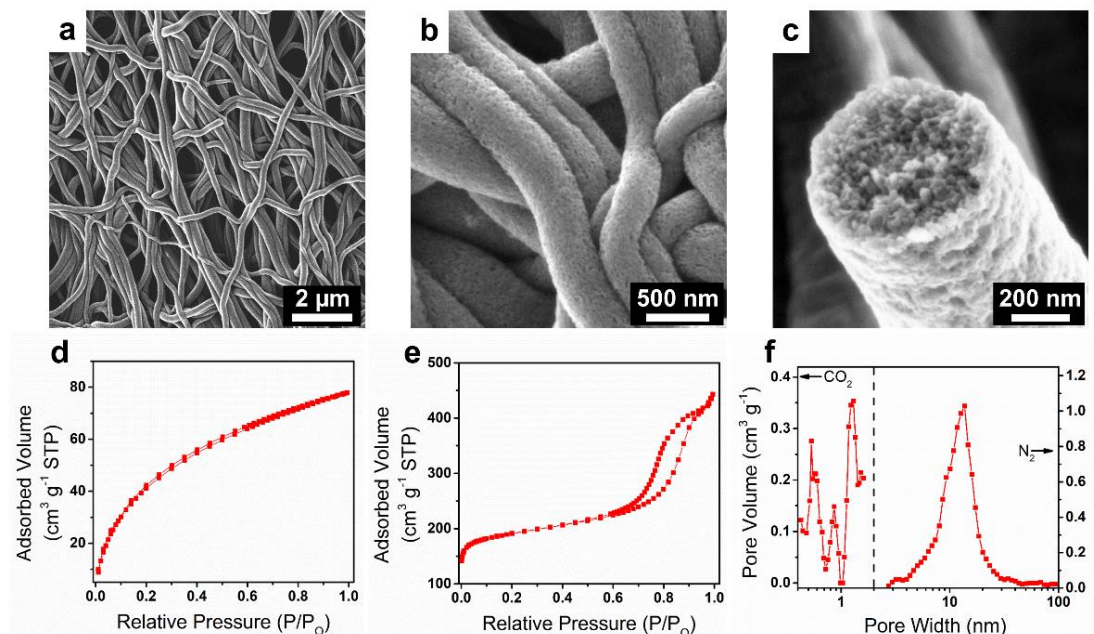


Figure 3.2. (a-c) Representative SEM images of PCF from PMMA-*b*-PAN after pyrolysis at 800 °C. (d) CO₂- and (e) N₂-physisorption isotherms. (f) Micropore and mesopore size distributions.

The coexistence of micropores, mesopores, and inter-fiber voids formed a hierarchical porous structure. The hierarchical porous structure provided dye ions with easy accessibility to surface sites in the fibers. Additionally, the pore interconnectivity was expected to facilitate dye ion diffusion and thus enhance the dye removal.

3.4.3 Dye removal by PCF

Considering the high surface area and interconnected hierarchical pores, PCF was used as an electrode for dye removal *via* electrosorption. The electrosorption was carried out in a methyl orange (MO) solution of 12.5 mg L⁻¹ by applying a bias voltage of 0.8 V across two PCF electrodes over a period of 24 h (**Figure 3.3a**). The concentration of MO at different time intervals was quantified using UV-vis spectroscopy. The light absorbance at 463 nm, a signature peak of MO, decreased continuously with electrosorption time (**Figure 3.3b**). Based on the dye concentration, the remaining dye percent in the solution and the loading of dye on PCF were plotted against time (**Figure 3.3c**).

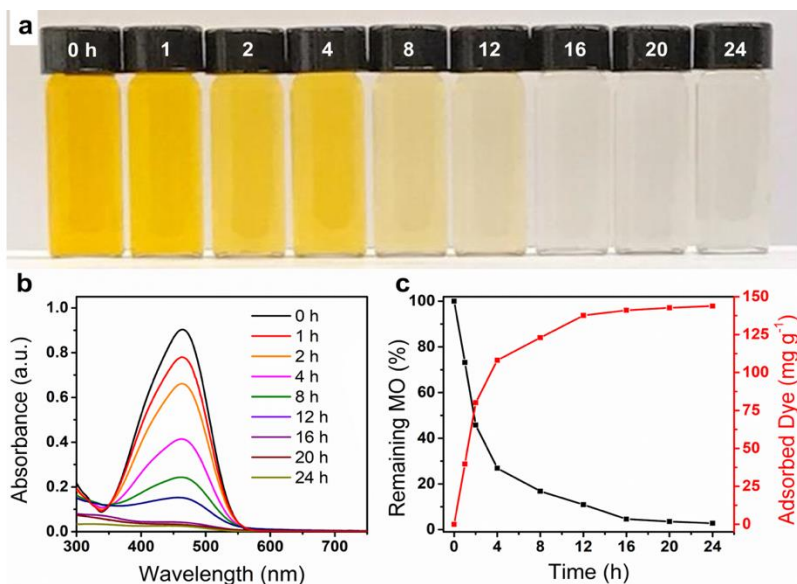


Figure 3.3. (a) Photograph of MO solutions after electrosorption for 0, 1, 2, 4, 8, 12, 16, 20, and 24 h (from left to right). The initial MO concentration was 12.5 mg L^{-1} . (b) UV-vis spectra of the solutions after electrosorption for 0-24 h. (c) The amount of MO adsorbed by PCF and the remaining MO% in the solutions as a function of electrosorption time.

The dye adsorption by the PCF involved several stages. Initially, the intense orange color faded rapidly. Within 1 h, PCF adsorbed $\sim 30\%$ of the dye ions in the solution. The electrosorption continued exponentially, adsorbing $\sim 75\%$ of the dye at 4 h. After 4 h, the electrosorption slowed down. The reduced electrosorption rate was attributed to two factors: (i) a lower concentration of MO in the bulk solution led to a slower diffusion rate;²⁵ (ii) most of the easily available active sites on the PCF were already occupied by the adsorbed ions. After 16 h, the solution became almost optically clear and only $\sim 5\%$ of the dye ions remained in the solution. The last 5% of the dye ions lasted for several hours. After 24 h, the remaining dye in the solution was $<1\%$ (**Figure 3.3a, c**).

3.4.4 Electrosorption kinetic analysis

The electrosorption mainly has four stages.⁵⁷ First, the dye ions diffuse across the liquid phase to the Helmholtz plane near the surface of PCF (*i.e.*, bulk diffusion or “mass transfer”). Second, the ions move across a boundary layer from the Helmholtz plane to the outer surface of PCF. The ions may be adsorbed directly onto external surface sites. Third, if the ions are not adsorbed onto the external surface sites, they continue to diffuse from the outer surface to the interior of PCF (also

called “intra-particle” diffusion⁴⁹ in the mesopores and micropores). Fourth, the electrical attraction between PCF and the oppositely charged ions leads to the adsorption of dye ions onto the internal active sites in the mesopores and micropores.¹⁹ Because the electrical attraction is an extremely fast process, it usually cannot be resolved in the kinetic analysis.

To understand the adsorption process, kinetic models are used to reveal the interplay between hierarchical pores and electrosorption. Based on the dye adsorption rates over time, the PCF electrosorption was modeled with pseudo-first order, pseudo-second order, and Weber-Morris models (**Figure 3.4**). The pseudo-first order model exhibited a poor fit of the adsorption data ($R^2 = 0.496$) while the pseudo-second order model showed a higher correlation ($R^2 = 0.982$) (**Figure 3.4a, b** and **Table S3.1**).

In conjunction, to identify the rate-limiting adsorption process, the Weber-Morris model was applied. The Weber-Morris model showed adsorption regimes consistent with the experimental data (**Figure 3.4c**). An exponential dye-adsorption trend in the first regime was attributed to the vast number of empty sites initially available when the voltage was applied, suggesting that bulk diffusion was not a limiting factor in the initial dye removal process.⁴⁹ The second stage showed a slower rate of adsorption due to increased repulsive forces exerted by the adsorbed ions on the surface.⁵⁸ By fitting the experimental data, the Weber-Morris model showed a linear correlation in the second regime ($R^2 = 0.996$) with an intercept of 75 mg g^{-1} on the q_t -axis.

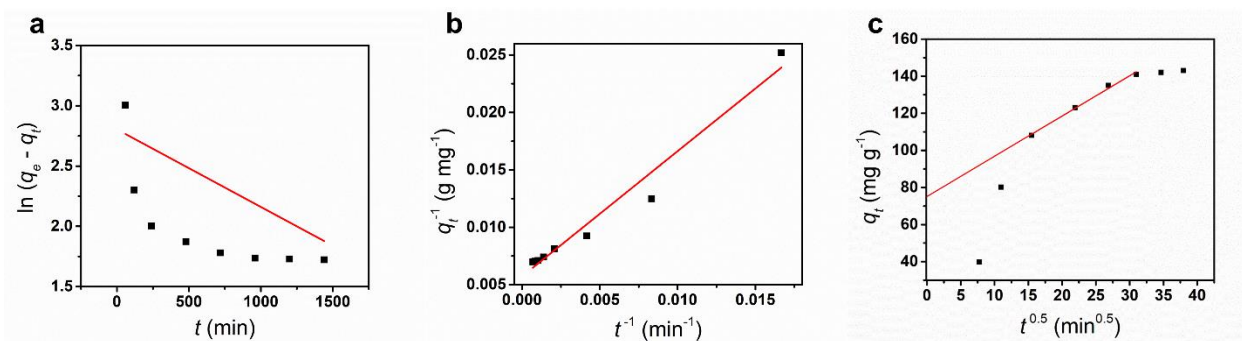


Figure 3.4. Electrosorption kinetic models for MO adsorption on PCF: (a) pseudo-first order, (b) pseudo-second order, and (c) the Weber-Morris model (intra-particle model).

According to the Weber-Morris model, the presence of the linear regime confirms the intra-particle diffusion of ions in the meso- and micro-pores.⁵⁹ The intra-particle diffusion allows for

accessibility of ions to all internal surface sites and contributes to a high adsorption capacity. Additionally, the positive intercept ($B > 0$) suggests that intra-particle diffusion is not the sole rate-limiting step.^{60,61} The intercept B is proportional to the thickness of the boundary layer.⁶⁰ Finally, in the third regime the diffusion slowed down as shown by the asymptotic adsorption trend. The slow ion diffusion was possibly due to (i) a reduction in the bulk dye concentration or (ii) reduced ion mobility in the micropores than in mesopores. Based on previous results with similar dye concentrations,⁵⁹ the turning point being between the second and third regime indicated that the mesopores and micropores were interconnected and accessible to the dye ions. The electrosorption behavior of our PCF underlines the importance of interconnected hierarchical pores for electrostatic dye removal. Furthermore, other reports also suggest that carbon fibers^{34,35} are a superior adsorption material due to the morphology.

3.4.5 Adsorption isotherm

Isotherm adsorption models were used to further understand the electrosorption, relative surface energy, maximum equilibrium adsorption capacity, and effects of the hierarchical interconnected pores (**Figure 3.5**). The electrosorption was modeled at varying initial MO concentrations from 6.25 to 1000 mg L⁻¹ at room temperature. The wettability of PCF towards aqueous solutions was excellent due to oxygen- and nitrogen-containing functional groups on the carbon fiber surfaces.^{44,59} This characteristic allowed for the infiltration of the aqueous electrolyte solution into the hierarchical porous matrix. The equilibrium loadings of MO on PCF were fit with respect to the initial concentrations using the Langmuir and Freundlich isotherm models (**Figure 3.5**). Based on non-linear and linear fitting, the Langmuir model described the data better than the Freundlich model, suggesting that the energy levels of the adsorption sites on the PCF were uniform.

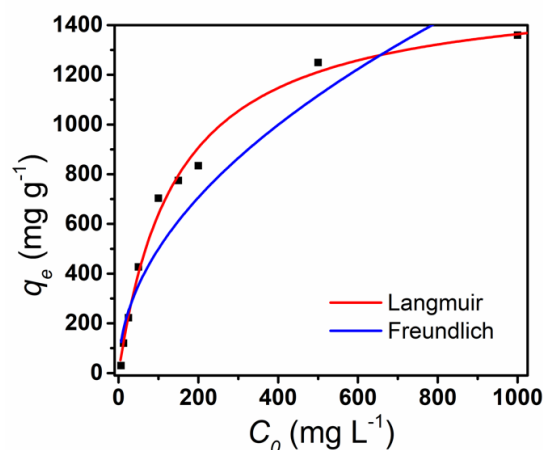


Figure 3.5. Equilibrium adsorption of MO on PCF over a concentration range of 6.25 to 1000 mg L⁻¹ using Langmuir and Freundlich isotherms.

The linear fitting of the Langmuir model (**Table S3.2**) showed high correlation ($R^2 = 0.998$) when the first isothermal point (6.25 mg L⁻¹) was ignored. The reciprocal of the intercept with an appropriate propagation of error calculation gave $q_{e,max} = 1690 \pm 14$ mg g⁻¹ where $q_{e,max}$ is the theoretical maximum absorbance in mg g⁻¹; similarly, the ratio of the intercept to slope gave $K_L = (6.1 \pm 0.5) \times 10^{-3}$ L mg⁻¹. The non-linearized form modeled the range of concentration from 6.25 to 1000 mg L⁻¹ (**Figure 3.5**) with a high correlation ($R^2 = 0.999$). The non-linear model fitting parameters were $q_{e,max} = 1560 \pm 60$ mg g⁻¹ and $K_L = (6.9 \pm 0.7) \times 10^{-3}$ L mg⁻¹. If the first isothermal point was ignored as it was in the linear model, then the non-linear fit parameters are, $q_{e,max} = 1560 \pm 60$ mg g⁻¹ and $K_L = (7.0 \pm 0.7) \times 10^{-3}$ L mg⁻¹, without any significant difference from the initial linear fit (**Figure S3.2**).

The exponential Freundlich model yielded a fit ($R^2 = 0.929$) of the data much poorer than the Langmuir model (**Figure 3.5**). The model fitting parameters were $K_F = 88.6$ and $b_f^{-1} = 0.716$. Noting, the b_f^{-1} value for Freundlich relates the relative correlation of homogenous ($b_f^{-1} > 0.5$) and heterogeneous ($b_f^{-1} < 0.5$) surface energies. The $b_f^{-1} > 0.5$ indicated equivalent energy levels of the adsorption sites, in agreement with the underlying assumption of the Langmuir model. Additionally, the linear forms (**Figure S3.2**) also showed poor modeling of the experimental data ($R^2 = 0.895$), which indicated that Freundlich does not represent well the PCF electrosorption. Since the experimental data was well described by the Langmuir model, it was reasonable to believe that this model effectively depicts the electrosorption process for the PCF.

Several key insights were obtained from the well fit Langmuir model, which suggested mechanistic interpretations of the electrosorption process. For example, the separation factor R_L describes the nature of the adsorption process where $0 < R_L < 1$ is favorable (*i.e.* reversible and nonlinear).⁶² For the PCF, R_L was 0.931 as calculated from eq. 3.13, indicating that the adsorption process was favorable (**Table S3.3**). The favorable adsorption process contributed to the PCF maximum adsorption of 1360 mg g⁻¹ (**Figure 3.5**), reaching ~87% of the theoretical maximum monolayer adsorption ($q_{e,max}$) of 1560 mg g⁻¹ at equilibrium based on the non-linear Langmuir model fit (**Figure 3.5**). Contributed from the hierarchy of inter-fiber macropores, mesopores, and micropores of PCF, the experimental maximum represented a much higher percentage of the theoretical maximum than other reported carbon materials, *e.g.*, carbon nanotubes (149 mg g⁻¹, 38% of maximum),⁶³ reduced graphene oxide (300 mg g⁻¹, 33% of maximum),⁶⁴ and graphene-carbon nanotube hybrid (237 mg g⁻¹, 48% of maximum).⁶⁵ Additionally, the PCF show high adsorption rates in comparison with other active materials (**Table S3.4**).

Combining the Langmuir model, Freundlich model, and Weber-Morris model, the electrosorption process provides consistent conclusions. First, the high surface area of the PCF allows for the high capacity and rapid saturation of surface adsorption sites.^{29,61} Second, relating the Weber-Morris model and the Langmuir model, the experimental data indicates that mass transfer is not the rate-limiting step and the high capacity is attributed to the interconnectivity of the hierarchical pores. Third, the surface of PCF is rather homogeneous for the dye adsorption. The homogeneity of the PCF surface is validated by both, the high correlation coefficient of the Langmuir model, and the b_f^{-1} value of the Freundlich model. Thus, the electrosorption of dye ions on PCF behave as a high performance electrosorption material with a relatively large boundary layer on a relatively homogeneous surface, rather than electrostatic or electrochemical interactions with a heterogeneous surface with various surface functional groups.

3.4.6 Recyclability

Recyclability is an important figure-of-merit of materials for water purification. Because of the reversible mechanism of electrosorption, the dye ions on the carbon surface can rearrange themselves and facilely desorb from the surface.⁶⁶ PCF showed high recyclability after 10 cycles for a total duration of 240 h (**Figure 3.6**). After electrosorption, each solution of the 10 cycles appeared clear (**Figure 3.6a**). UV-vis spectroscopy was used to quantitatively measure the

concentration of MO. Each solution contained <1% remaining MO, and the dye loading on PCF varied <0.5 mg g⁻¹ (Figure 3.6b). The first cycle showed an adsorption loading of 149 mg g⁻¹ and after 10 cycles the adsorption loading varied <0.5% (Figure 3.6c).

The low loading loss indicates excellent recyclability of PCF for the reversible electrosorption process (Figure S3.3). The two-electrode system set-up allows for an 0.8 V bias leading to a rapid uptake of ions, which marks the decrease in overall current (Figure S3.3a). For the recyclability of the electrodes, however, the same electrodes were placed in deionized water. The previously captured ions desorb from the carbon fiber surfaces and re-solvate into the new solution, which markedly showed a decay in current density approaching 0 A g⁻¹ (Figure S3.3b). Compared with other methods for high-capacity dye removal, electrosorption provides recyclability and produces no secondary waste.^{14,67}

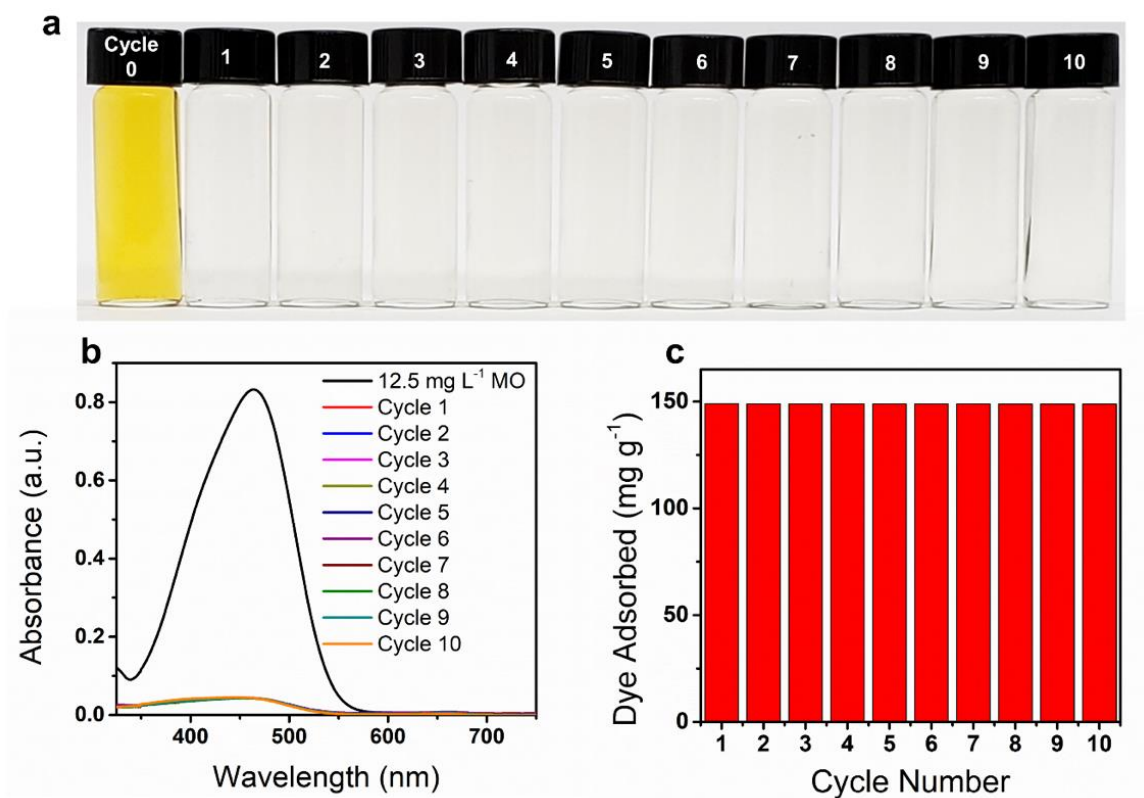


Figure 3.6. Regeneration and reusability of PCF. (a) A representative initial MO solution and ten resultant solutions after electrosorption for 24 h at 0.8 V using the same PCF electrode. PCF was regenerated after each cycle. (b) UV-vis spectra of the corresponding solutions. (c) The regeneration capabilities of PCF for dye removal over the 10 cycles.

3.4.7 Multiple dye filtration

For multiple dye ion electrosorption, solutions of MO and MB at equal concentrations were treated with symmetric PCF electrodes under 0.8 V for 24 h (**Figure 3.7**). Since the dye ions have equal concentrations but opposite charges, they were analogously adsorbed on the respective electrodes, that is, MO on cathode and MB on anode (**Figure S3.1**). The adsorption of MO and MB were shown by the drastic decrease in absorbance intensity at 463 nm and 664 nm, respectively (**Figure 3.7a**). Compared to other materials such as flow-through membranes, which typically provide faster adsorption rates^{68,69} but sometimes at the cost of efficiency and recyclability, the electrosorptive PCF herein provides high rate, high efficiency, and high recyclability.⁷⁰ Notably, the multiple dye solutions contained counter ions for each salt, in this case, Na and Cl.

The system can be configured to selectively remove one type of pollutant (**Figure 3.8**). For instance, switching the anode to a different conductive material (*e.g.*, conductive copper wire) enabled the adsorption of MB only (**Figure 3.8b**). This practice illustrates the advantage of electrosorption being capable of removing either one or both charged species from a solution. Note that the selective removal is based on ionic charge, which has the benefit from separating cation and anions, though unlikely has the ability to separate ions of the same charge (*i.e.*, a cation and another cation). Previous studies show adsorption efficiency benefit from a supporting electrolyte to provide higher conductivity than the dye solutions.⁶⁹ Supporting electrolyte of NaCl was added to reach a final concentration of 100 mg L⁻¹ to ensure sufficiently high conductivity of the solution. Although the Na⁺ and Cl⁻ ions were present in the solution, all adsorption rates were calculated by UV-vis spectrometry. Thus, competition by the electrolyte was accounted for in the electrosorption rate calculations.

The selective binding of the pollutants provides potential future applications for filtration and water remediation. The study herein is based on symmetrical electrodes of PCF. The selective absorption of MB shows a facile control over the removal process and the separation of anion and cationic dyes is achieved (**Figure 3.8**). Note that the selective removal is based on ionic charge, that is, separating cation and anions, but PCF unlikely discriminates ions having the same charge *via* electrosorption. We speculate that asymmetrical electrodes can provide a means for ionic species separation of opposite charges in the future.

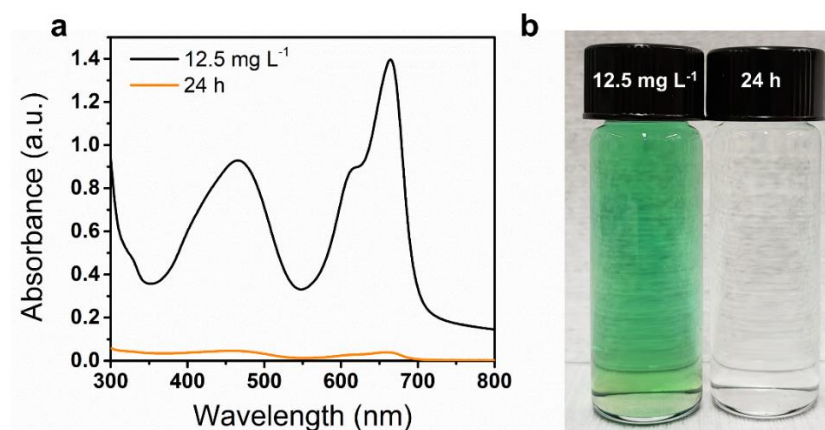


Figure 3.7. (a) UV-vis spectra and (b) optical photograph of multiple dye electrosorption by PCF. The MO and MB initial concentration was 12.5 mg L^{-1} .

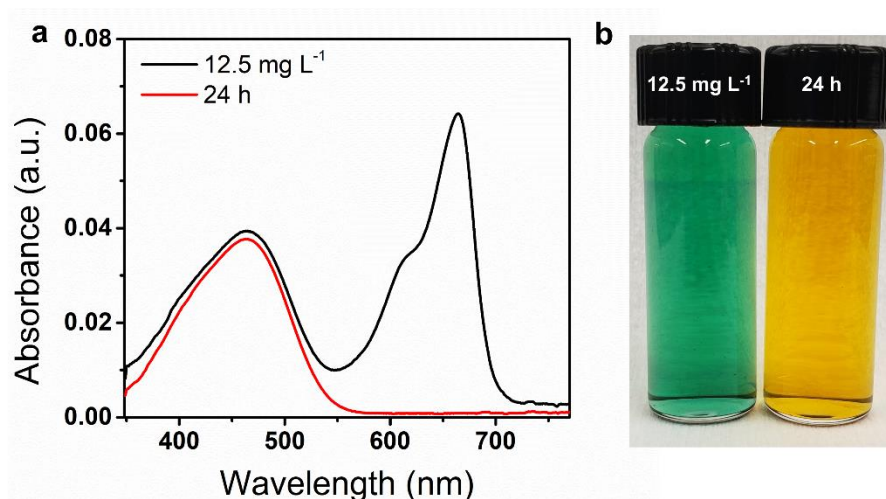


Figure 3.8. (a) UV-vis spectra and (b) optical photograph of selective dye adsorption by PCF. The MO and MB initial concentration was 12.5 mg L^{-1} .

3.5 Conclusions

Herein we have employed PMMA-*b*-PAN derived hierarchical PCF to electrosorb dye contaminants from water. PCF had a high surface area and narrowly distributed pore widths. The maximum loading of methyl orange dye on PCF achieved 1360 mg g^{-1} , more than the weight of the active material (PCF) itself. The excellent electrosorption performance of PCF was attributed

to the interconnected hierarchical pores, which provided a high effective surface area for electrosorption. The Weber-Morris model described well the adsorption behaviors of PCF, suggesting that the interconnected pores were beneficial for intra-fiber diffusion in the electrosorption process.

In conjunction, the adsorption profiles were well fit well by the Langmuir model, indicating that the dye ions diffused easily and continuously from the exterior to mesopores and to micropores. With a symmetrical PCF electrode configuration, multiple dyes were adsorbed simultaneously. With an asymmetrical electrode configuration, PCF showed selective dye removal and exhibited control over anionic and cationic uptake. Therefore, PCF represents a promising material for wastewater treatment, as well as for other applications such as desalination,⁷¹ gas sequestration,⁷² and energy storage.^{73–76} This study not only offers a novel porous carbon material for electrosorptive dye removal, but also provides insights into the mechanism for charged dye removal in hierarchical porous structures, enabling future design of porous materials for filtration applications.

3.6 Supporting Information

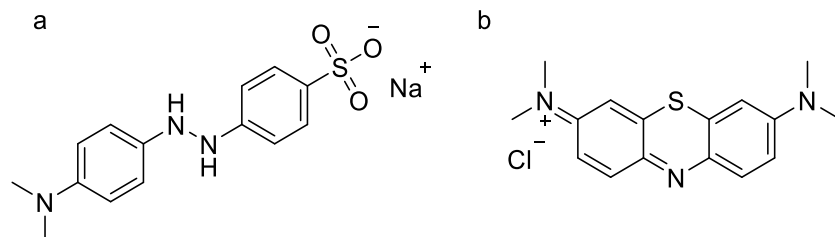


Figure S3.1. Structures of (a) methyl orange and (b) methylene blue.

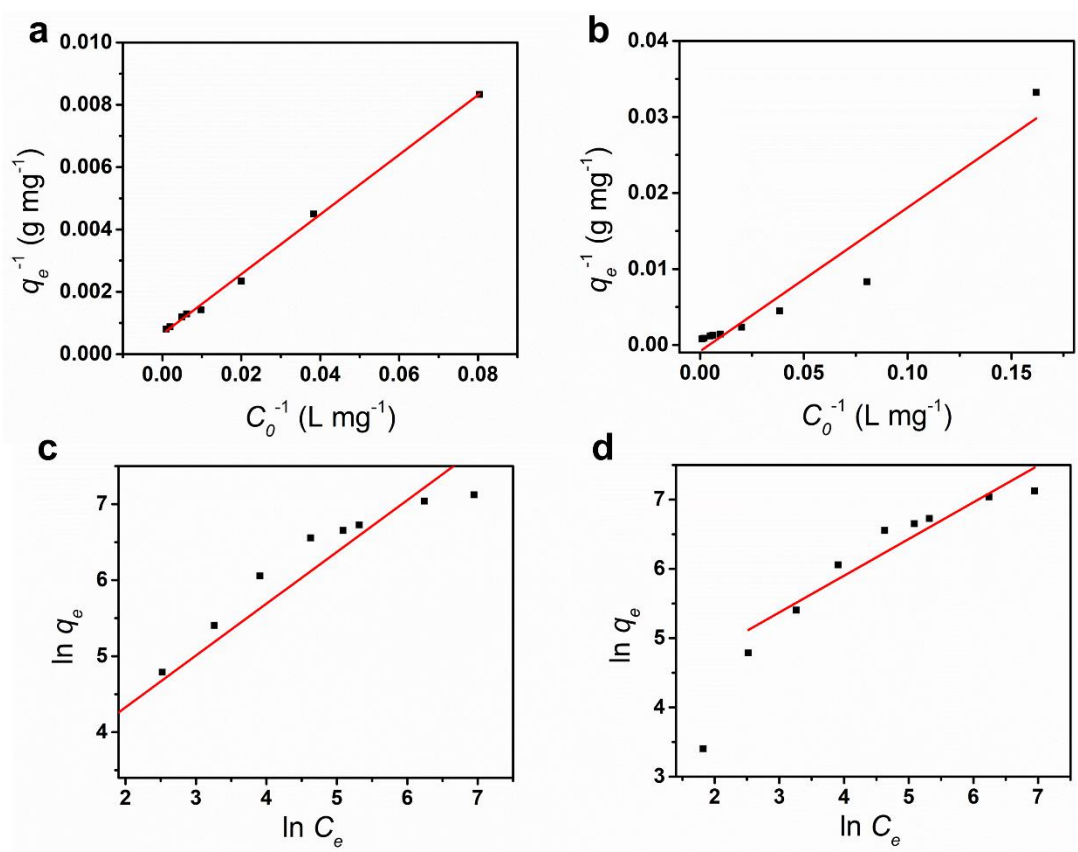


Figure S3.2. Fitting of linearized forms of the Langmuir and Freundlich model. (a) Langmuir model excluding the first isothermal point at 6.25 mg L⁻¹; (b) Langmuir model including the first

isothermal point at 6.25 mg L⁻¹; (c) Freundlich model excluding the first isothermal point at 6.25 mg L⁻¹; (d) Freundlich model including the first isothermal point at 6.25 mg L⁻¹.

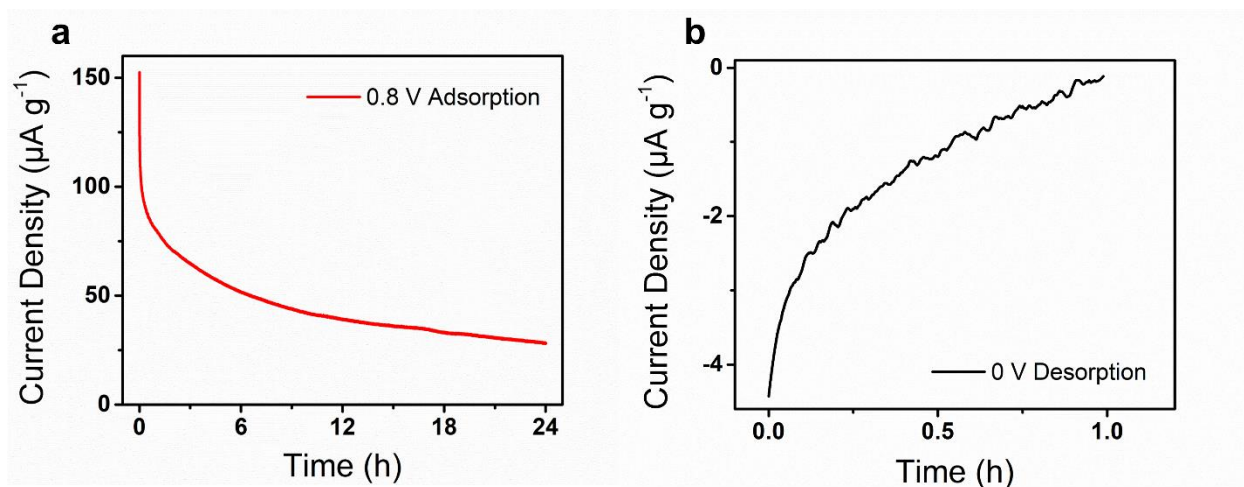


Figure S3.3. (a) Adsorption current density at a constant voltage of 0.8 V and (b) desorption current density by applying a bias of 0 V using an external source.

Table S3.1. Kinetic parameters of pseudo-first order, pseudo-second order, and Weber-Morris models.

Pseudo-first order				Pseudo-second order			Weber-Morris		
q_e (mg g ⁻¹)	k_1 (min ⁻¹)	$q_{e,cal}$ (mg g ⁻¹)	R^2	k_2	$q_{e,cal}$ (mg g ⁻¹)	R^2	k_i	B (mg g ⁻¹ min ^{-0.5})	R^2
423	6.42	16.5	0.496	2.98×10^{-5}	175	0.982	2.17	75	0.996

Table S3.2. Parameters of the linear fitting of Langmuir and Freundlich isotherms.

Langmuir (8 points)			Freundlich (8 points)		
K_L (L mg ⁻¹)	$q_{e,max}$ (mg g ⁻¹)	R ²	K_F	b_f	R ²
0.0061	1690	0.998	1.33	0.52	0.895

Table S3.3. Parameters of the non-linear Langmuir and Freundlich isotherms.

Langmuir				Freundlich		
K_L (L mg ⁻¹)	$q_{e,max}$ (mg g ⁻¹)	R_L	R ²	K_F	b_f	R ²
0.0069	1560	0.931	0.999	88.6	0.716	0.929

Table S3.4. Quantitative comparison over four adsorption systems, a co-precipitation system, and a nano-filtration system.

Materials ^a	Dyes	Surface area (m ² g ⁻¹) ^b	Concentration range (mg L ⁻¹)	Max adsorption (mg g ⁻¹)	pH	Percentage of removal	Ref.
AC-Bagasse	Acid blue 80	1433	1050	391	7.4	-	S1
Chitosan	Acid orange	-	1130	922.9	4	-	S2
Charred dolomite	Dye E-4BA	36	400-1000	950	8	90%	S3
Green alga	Reactive red 5	-	20-800	555.6	2	85%	S4
Calcium chloride	Blue Bezaktiv S-GLD	-	40	-	5-9	94%	S5
CMCNa/PP thin film composite	Congo Red,	-	100	-	6.8	99.9%	S6
PCF	Methyl orange	780	12.5-1000	1360	7.2	96%	This work

^a AC-Bagasse, chitosan, charred dolomite and green alga were utilized for dye adsorption. Calcium chloride was used as co-precipitation agent, and CMCNa/PP composite was a nanofiltration membrane.

^b surface areas were characterized by N₂ physisorption.

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Chapter 4. Reduction in Water Vaporization Enthalpy by Block Copolymer-Based Porous Carbon Fibers

This chapter has been adapted from a submitted manuscript by Serrano, J. M., Liu, T., Croft, Z., Cao, K., Khan, A., Xu, Z., Nough, E., Cheng, S., and Liu, G.

4.1 Abstract

Solar desalination, a technique converting solar irradiation to heat for evaporating saltwater and generating freshwater, has garnered much attention because of the ever-growing global demand for potable water. Herein, we utilize block copolymer-based porous carbon fibers with well-controlled porous structures to investigate the latent heat reduction in mesopores and micropores. The porous carbon fibers achieve high energy efficiencies and solar desalination rates up to $3.8 \text{ kg m}^{-2} \text{ h}^{-1}$ under 1 sun irradiation, owing to the >99% light absorption across the solar spectrum and reduced vaporization enthalpy of pore-confined water. The nano-confinement effect of pores is evaluated by measuring evaporation enthalpies and rates for morphologically tailored carbon fibers with pore sizes ranging from ~ 1 to ~ 22 nm. Our results show a continuous reduction in enthalpic energy of up to 50% as mesopore size decreases to ~ 10.7 nm, and then less reduction of only 14% with a further decrease in micropore size to < 1 nm. The mesopores exhibit significantly enhanced evaporation rates compared with micropores due to the nanoscale confinement-related enthalpy reduction and water transport. This study provides insight into nano-confinement effects with well-controlled pore sizes and contributes to further understanding and design of porous materials for future environmental applications.

4.2 Introduction

A major challenge for the growing global population is the disparity between freshwater demand and supply. Although brackish and sea water is abundant, the energy required for desalination using current methods prevents wide access to potable desalinated water. Many technologies are

under development to combat this problem by enhancing desalination efficiency.^{1, 2} Distillation and similar thermal-based methods produce water through vaporization and recondensation, yet they suffer from limited energy efficiencies.³ Other systems, such as membrane-based reverse osmosis,⁴ consume comparatively less energy than the thermal-based methods,⁵⁻⁷ but experience other issues such as membrane biofouling, high working pressures, and intensive maintenance, in addition to large footprints and costly infrastructures.^{8, 9} Alternatively, solar desalination requires much lower energy input and less complex infrastructures.¹⁰⁻¹² Solar also provides off-grid and low-to-no waste production of potable water from high-salinity sources.^{13, 14} Thus, solar desalination has gained increasing popularity in confronting the aforementioned challenges faced by traditional systems, especially in regions with limited access to large-scale infrastructure.^{15, 16}

Solar energy provides a sustainable source for water vapor generation, but an effective solar desalination system demands both high light absorption and photothermal conversion efficiencies.^{17, 18} The literature has focused on strategies ranging from initial energy harvesting to final recondensation.¹⁹⁻²¹ For example, ultra-absorbers such as plasmonic nanoparticles highlighted the importance of solar-to-thermal energy conversion efficiency.²²⁻²⁴ Strategized materials such as thermal-concentration ceramics²⁵ and nanostructured gels,²⁶ addressed the issue of parasitic heat loss by localizing heat and reducing energy dissipation. Heat recovery was realized by coupling photonics with distillation to further mitigate energy loss.²⁷ These strategies highlight the rationales of increasing solar energy uptake and decreasing energy loss, all of which enhances solar desalination efficiency. However, another fundamental and yet important mechanism remains largely underdeveloped in the minimization of the inherent energy requirement for the phase change of water from liquid to vapor.^{17, 28}

Owing to the large vaporization enthalpy of water, even a ultra-high efficient system - without any latent heat reduction - could only achieve a theoretical maximum evaporation rate of $1.6 \text{ kg m}^{-2} \text{ h}^{-1}$ under 1-sun irradiation.³ New technologies are under development to address this challenge by lowering the energy required for vaporization.²⁹⁻³¹ Previous experimental and simulation studies also point towards the potential for achieving high desalination efficiency using a nano-confinement approach, which reduces the intermolecular interactions between adjacent water molecules and thus water density.³²⁻³⁵ Despite numerous reports using porous materials such as carbon foam,³⁶ and pyrolyzed biomasses,³⁷⁻³⁹ for solar-thermal desalination, the differing effects of mesopores and micropores on nano-confinement of water remain unclear.⁴⁰⁻⁴² To this end, we

designed a system with controllable pore sizes, utilizing our recently developed block copolymer-based porous carbon fibers (PCFs), to elucidate the relationship between nano-confinement and water vaporization enthalpy.

Our judiciously selected block copolymer precursor, poly(methyl methacrylate)-*block*-poly(acrylonitrile) (PMMA-*b*-PAN), provides a controlled, template-free method for producing PCFs *via* sequential electrospinning, oxidation, and pyrolysis (**Figure 4.1**). Owing to the unique capability of microphase separation, the block copolymer forms well-defined mesoscale structures for formation into mesopores. The size of the mesopores is highly uniform, as governed by the block copolymer molecular weight and composition. In addition, the intrinsically semi-crystalline PAN develops well-controlled micropores during the carbonization process. Therefore, PMMA-*b*-PAN provides an exceptional platform for investigating the effects of mesopores and micropores on solar water vaporization. PCFs are expected to exhibit excellent solar desalination efficiency because: (i) PCFs absorb >99% of wavelengths in the solar spectrum, lending them to high solar energy harvesting capability; (ii) electrospinning creates inter-fiber macropores for rapid transport of water from the bulk to the inter-fiber space and the interconnected meso- and micro-pores; (iii) the nano-confinement accelerates water evaporation by decreasing vaporization enthalpy; and (iv) PCFs have enhanced heat transfer contained by thermal diffusion within the fiber mat. Consequently, the well-defined, and tunable pore structures allow for an unprecedented opportunity to experimentally examine the evaporation behavior of water under varying nano-confinement conditions.

With well-tuned pore sizes from ~0.6 to 21.6 nm, our measurements showed that for block copolymer-derived PCFs, the vaporization enthalpy diminished to ~43% of the value for bulk water with decreasing mesopore sizes. The water evaporation rate reached a maximum of 3.8 kg m⁻² h⁻¹ under 1 sun irradiation, ~9.5 times higher than the evaporation rate of bulk water. In contrast, PAN homopolymer-derived carbon fibers (CFs), with micropores of <2 nm and no mesopores, only reduced the latent heat for water vaporization by ~14% and was significantly inferior for solar desalination. The nano-confinement provided by the PCFs enables facile desalination and deepens the understanding of latent heat reduction induced by confinement (**Figure 4.1**). This work serves as a useful guide for material design in future environmental applications.

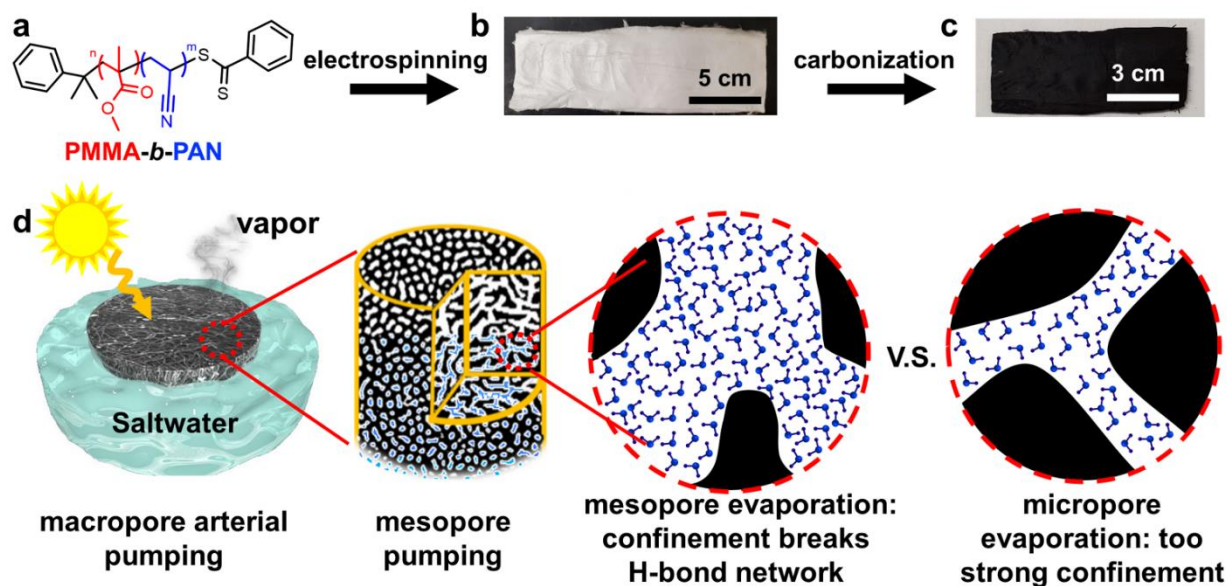


Figure 4.1. Scheme of block copolymer-based porous carbon fibers for solar desalination. (a) PMMA-*b*-PAN block copolymers were synthesized and electrospun to (b) polymer fiber mats and then converted to (c) porous carbon fibers *via* carbonization. (d) The fibers were semi-submerged in saltwater. Water travelled through the inter-fiber macropores via arterial pumping and then toward the interiors of the fibers *via* mesopore pumping. The interior mesopores and micropores pose different nano-confinement effects on water.

4.3 Results and Discussion

4.3.1 Design, synthesis, and characterization of porous carbon fibers

Using reversible addition-fragmentation chain transfer (RAFT) polymerization, we synthesized PAN homopolymers and PMMA-*b*-PAN block copolymers, based on our previous report.⁴³ The molecular weight and composition of PMMA-*b*-PAN control the surface area and mesopore size distribution of PCFs. In general, high molecular weight and volume fraction (ϕ) of PMMA results in large mesopore sizes. Thus, three PMMA-*b*-PAN polymers were synthesized with number average molecular weights (M_n) of 108-*b*-44, 59-*b*-36, and 41-*b*-66 kDa (Figure S4.1) to produce three types of PCFs, designated PCF-A, PCF-B, and PCF-C, respectively (**Table 4.1**). As a control,

PAN with $M_n = 46$ kDa was also synthesized to produce microporous CFs. As reported previously,⁴⁴ PAN with M_n in the range of 13 to 215 kDa produced CFs with similar properties.

Table 4.1. Characteristics of polymer precursors from RAFT polymerization

Polymer	M_n , PMMA (kDa)	M_n , PAN (kDa)	ϕ_{PAN}^a	PDI ^b	Corresponding Fibers
PAN	-	46	1	1.19	CF
BCP-A	108	44	0.29	1.17	PCF-A
BCP-B	59	36	0.37	1.15	PCF-B
BCP-C	41	66	0.59	1.10	PCF-C

^a Volume fraction of PAN

^b Polydispersity index

The polymers were electrospun into fibers, which were then sequentially oxidized in air and pyrolyzed under N_2 to produce PCFs and CFs (**Figure 4.1c**). The fiber bundles exhibited nonuniform inter-fiber distances (**Figure 4.2a-d**). Since the capillary height is inversely proportional to the radius of a capillary, the inter-fiber gaps can act as channel-like macropores to efficiently transport water for desalination, analogous to the hydrophilic macroporous channels that benefited water transport *via* arterial pumping in a previous report.⁴⁵

In addition to the macropores, PCFs displayed distinct ubiquitous mesopores, both on the skin surfaces (**Figure 4.2a-c**) and in the cross-sections (**Figure 4.2e-g**). The PAN block served as the primary carbon source during pyrolysis, whereas the PMMA block acted as a sacrificial component to produce well-dispersed, uniform mesopores *via* thermodynamically driven microphase separation and thermal decomposition.⁴³ Contrastingly, the PAN-derived CFs were devoid of any visible mesopores (**Figure 4.2d, h**).

Gas physisorption analysis revealed the pore widths and surface areas of the PCFs and CFs (**Figure 4.3**). The N_2 and CO_2 isotherms of all PCFs exhibited type IV and I characteristics, respectively, as defined by the International Union of Pure and Applied Chemistry (IUPAC).⁴⁶

Specifically, the N₂ sorption of PCFs showed hysteresis at $0.6 < P/P_0 < 0.9$, indicating the presence of mesopores (**Figure 4.3a**). On the other hand, the isotherms of CFs had type II and type I characteristics for N₂ and CO₂ adsorption respectively, suggesting the absence of mesopores but the presence of micropores. Nevertheless, the similar type I isotherms of CO₂ sorption signified that both PCFs and CFs contained micropores of similar pore widths (**Figure 4.3b**).

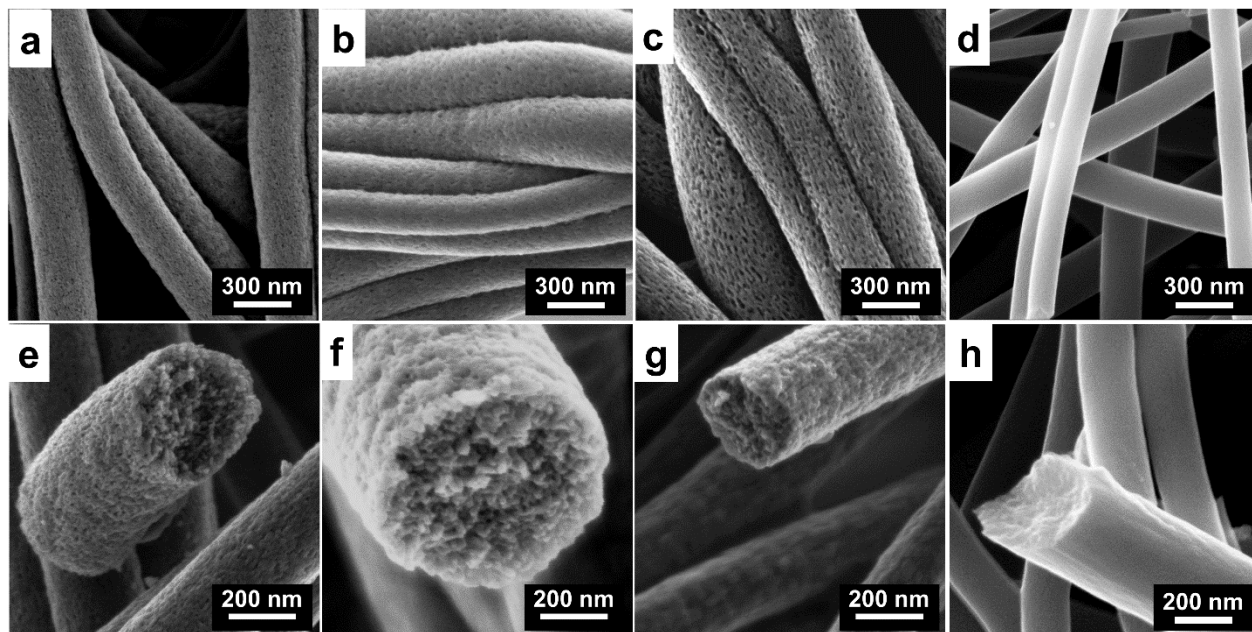


Figure 4.2. Representative SEM images of the outer surface (a-d) and cross-section (e-h) of (a, e) PCF-A, (b, f) PCF-B, (c, g) PCF-C, and (d, h) CF.

Using non-local density functional theory (NLDFT),⁴⁷ the pore width distributions were calculated (**Figure 4.3c**).⁴³ During carbonization, the carbon matrices of all PCFs and CFs developed micropores in trimodal peaks centered at ~ 0.58 , 0.86 , and 1.2 nm (**Figure 4.3c**).⁴⁸ PCF-A, PCF-B, and PCF-C also showed unimodal mesopore peaks at 21.6 , 14.7 , and 10.7 nm, respectively. The pore widths in the range of ~ 0.5 - 22 nm allowed for investigating the effects of pore-width effects on water vaporization (**Table S4.1**).

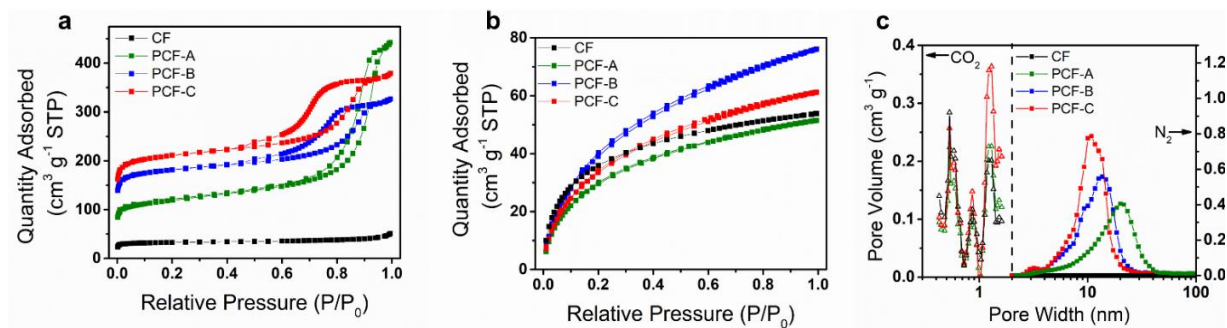


Figure 4.3. (a) N₂ and (b) CO₂ physisorption isotherms and (c) pore width distributions of PCF-A, PCF-B, PCF-C, and CF.

4.3.2 Solar desalination with PCFs

Using PCFs and CFs with different pore-size distributions, the effects of nano-confinement on solar desalination performance were studied. After pyrolysis, all PCFs and CFs absorbed >99% of the solar spectrum wavelengths (**Figure 4.4a**). The fibers were placed at the water-air interface of saltwater (35 g L⁻¹ NaCl), supported with a floating cork. Under 1 sun irradiation, weight loss due to water evaporation was tracked over time. The measured change in water mass over about six hours revealed an increasing evaporation rate in the order of blank water, CF, PCF-A, PCF-B, and PCF-C (**Figure 4.4b**). The evaporation rates were normalized to the fiber mat surface area exposed to sunlight (*i.e.* geometrical area) and are reported in units of water evaporated per unit area per unit time (**Figure 4.4c**). PCF-C displayed the highest desalination rate of 3.8 kg m⁻² h⁻¹.

The energy efficiency (η) for solar vapor generation was calculated according to the following equation:

$$\eta = (mH_{\text{vap}})/(C_{\text{opt}} P_0) \quad (4.1)$$

where m is the mass flux, H_{vap} is the vaporization enthalpy of water, C_{opt} is the optical concentration on the absorber surface (without any concentration, $C_{\text{opt}} = 1$), and P_0 is solar irradiation intensity (1-sun 1000 W m⁻²). To calculate the energy efficiency, H_{vap} was estimated by both differential scanning calorimetry (DSC) and dark-field evaporation (Figure S4.2). The highest performing fibers (PCF-C) reached an energy efficiency of ~94% (based on the enthalpy measured by DSC, *vide infra*).

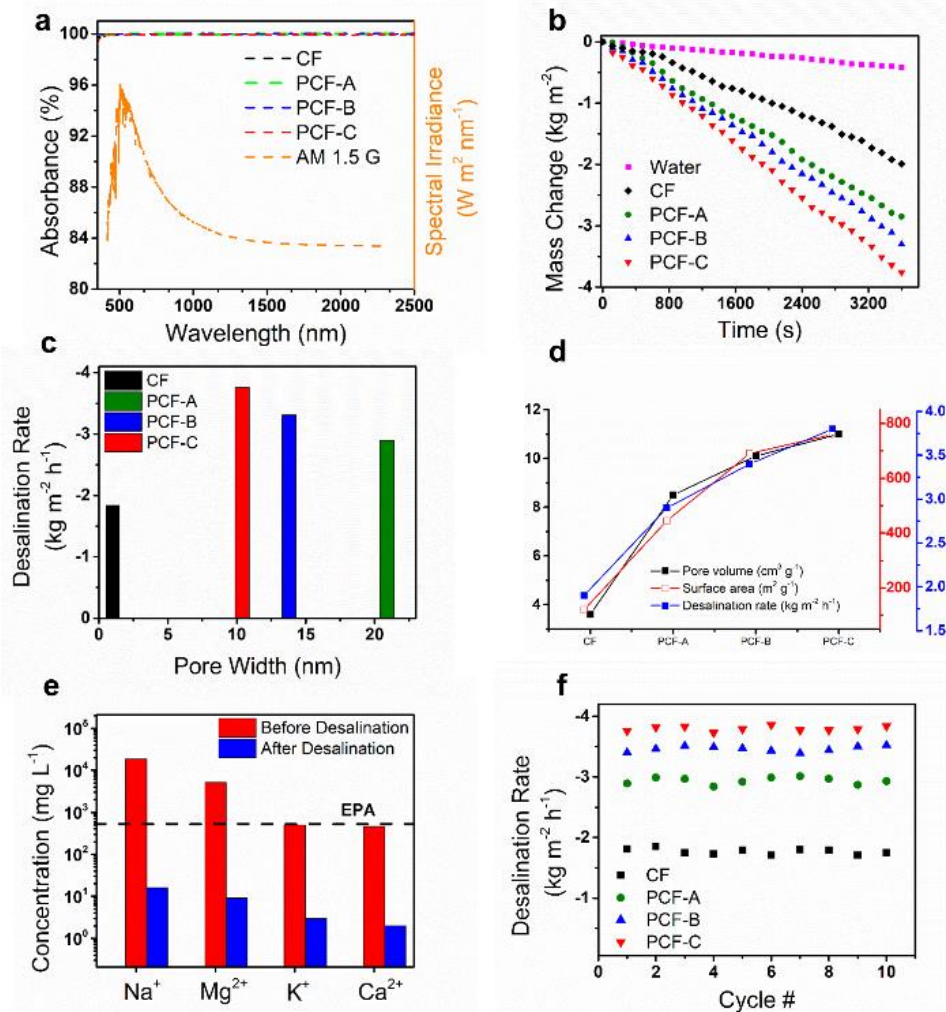


Figure 4.4. (a) UV-vis absorption spectra of PCFs and CFs overlaid with AM 1.5 G solar irradiation spectrum. (b) Mass loss over time under 1-sun irradiation using PCFs and CFs as solar desalination materials, compared to a water only cell (labelled as “water”). (c) Desalination rate against the average pore width of PCFs and CFs. (d) Desalination rate against the surface area and pore volume of PCFs and CFs. (e) ICP-MS analysis of four common ions in saltwater before and after desalination using PCF-C. The black dashed line highlights the U.S. Environmental Protection Agency (EPA) safe drinking water level. (f) Reusability of PCFs and CFs over 10 cycles (2 h per cycle).

The desalination rate was positively correlated with the pore volume and surface area calculated using BET theory (**Figure 4.4d**). To reveal the purity of evaporated water, inductively coupled

plasma mass spectrometry (ICP-MS) was used to probe the salinity of four common ions, including Na^+ , Mg^{2+} , K^+ , and Ca^{2+} , before and after desalination. The pre-evaporated saltwater solution contained $1.9 \times 10^3 \text{ mg L}^{-1}$ of Na^+ , $6.5 \times 10^3 \text{ mg L}^{-1}$ of Mg^{2+} , $5.7 \times 10^2 \text{ mg L}^{-1}$ of K^+ , and $5.1 \times 10^2 \text{ mg L}^{-1}$ of Ca^{2+} . However, the distillate after evaporation showed orders-of-magnitude reduction in ion concentrations (**Figure 4.4e**). The concentrations of Na^+ , Mg^{2+} , K^+ , and Ca^{2+} were all below 11 mg L^{-1} , meeting the standard of drinking water set by the U.S. Environmental Protection Agency (**Figure 4.4e**).⁴⁹

Practical solar desalination requires the solar absorbers to be robust and sustainable under continuous irradiation in high saline water. The PCFs and CFs performance remained stable under irradiation, evident by their constant evaporation rates (**Figure 4.4f**). The vaporization rates were tested over ten cycles for each type of PCF and CF. During each cycle, fresh saltwater was refilled into the desalination testing cell and irradiated continuously. The PCFs also showed facile self-cleaning ability and negligible efficiency loss. When not in use, salts might precipitate along the exterior of the fibers. The ability for salt resistance or self-cleaning material directly impacts the continuous use of solar desalination systems.⁵⁰ However, once the fibers were placed in saline water, the salts quickly dissolved because the fibers were hydrophilic and the pores facilitated water transport to wet the fibers (Figure S4.4).

4.3.3 *Enthalpic reduction of water confined in PCFs*

The well-defined hierarchical pores in the PCFs permitted investigations into the influence of surface area, pore volume, and pore size on desalination, a fundamental understanding of which is crucial for designing future solar thermal materials. Water confined in the pores of PCFs and CFs were analyzed with differential scanning calorimetry (DSC) using a temperature scan from room temperature to 120°C under a heating rate of 10°C s^{-1} (**Figure 4.5a**). By integrating the heat flow vs. time, the enthalpy of water vaporization within the CFs and PCFs was estimated. The CFs showed an endothermic peak with an intensity of $\sim -10 \text{ W g}^{-1}$ at 89°C . The peak endothermic temperature further decreased in the order of PCF-A, PCF-B, and PCF-C, to 74°C , 71°C , and 52°C , respectively (**Figure 4.5a**). For PCF-A, PCF-B, and PCF-C, the peak heat flows decreased progressively to -7.7 , -7.8 , and -4.6 W g^{-1} (**Figure 4.5a**), corresponding to a vaporization enthalpy (H_{vap}) of ~ 1790 , 1480 , and 1160 J g^{-1} (**Figure 4.5b**), respectively.

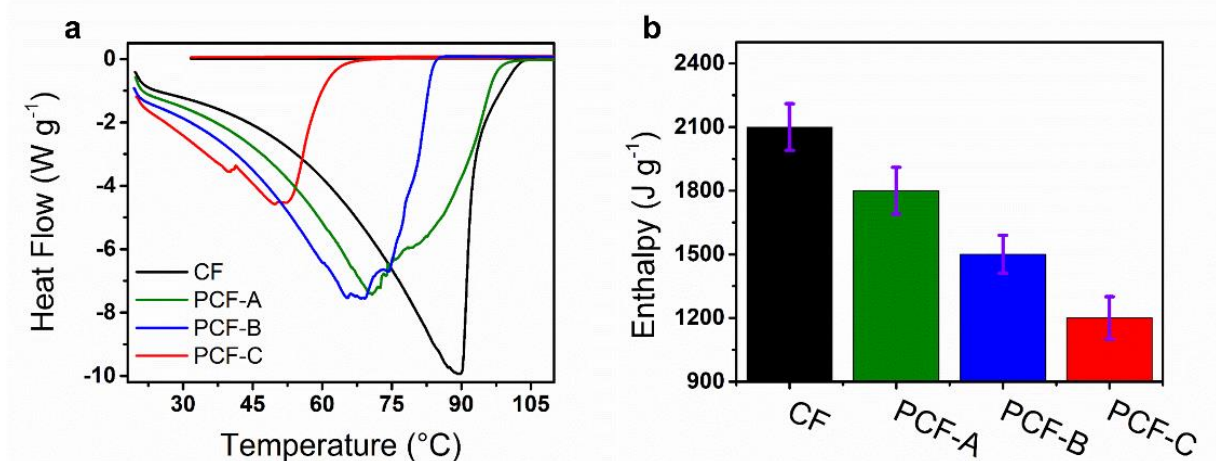


Figure 4.5. (a) Differential scanning calorimetry (DSC) traces for water confined in CFs and PCFs. (b) Equivalent water vaporization enthalpy calculated from the DCS curves. Error bars are standard deviations.

In addition, the mass of the water within the carbon fibers were monitored with DSC (Table S4.2). The soaked PCF fibers adsorbed $\sim 10\times$ their weight in water, which aligns with the combined pore volume estimates by CO₂ and N₂ physisorption. Based on the weight of the water and the integrated DSC trace, the enthalpy was directly estimated by the input of energy (J) into the system. Consistently, the PCF fibers showed a lower energy input for evaporation of water within the DSC pans (Table S4.2).

Hydrogen bonding is a major contributor to the cohesion among water molecules and the H_{vap} of water. Previous research into water-confinement shows hydrogen bond disruption in pores with widths < 100 nm.⁵¹ Previous studies into carbonized material with pores < 100 nm also attributed evaporation to reduced enthalpy.⁴¹ In this work, the CFs and PCFs conferred different confinement effects on water molecules. For bulk water, the vaporization enthalpy at 25 °C and standard pressure is ~ 2440 J g⁻¹. With inter-fiber distances and micropores in the CF the H_{vap} was reduced ~ 2090 J g⁻¹ which provided an estimation of enthalpy without mesopores. Upon the addition of mesopores, the surface area, pore volume, and confinement potential of the carbon fibers increased. The culminating factors of the hierarchical resulted in a larger reduction in H_{vap} which delves into two confinement factors: the disruption of the hydrogen bonding network of water molecules and the development of smaller capillary structures within the mesopores.⁵² In addition, the mesopores also contribute a tertiary beneficial factor in a lower the thermal diffusivity within

the PCFs (Figure S4.5). Notably, PCF-C had the smallest H_{vap} . The reduction in H_{vap} determined by DSC was also confirmed by dark-environment (dark-field) evaporation, with the CFs and PCFs following an identical trend (Figure S4.3). Owing to the mesopore-related reduction in H_{vap} , all PCFs displayed high solar desalination rates. The smaller the mesopores, the more reduction in H_{vap} observed and thus the higher solar desalination rates. However, this effect diminished in the CFs that had only micropores. Notably, both CFs and PCFs possessed macropores (inter-fiber voids due to fiber processing), which aided water transport.

The PCFs with mesopores speed up water evaporation (**Figure 4.5a**) by suppressing hydrogen bonds to the extent that the vaporization enthalpy of water is significantly reduced, but at the same time, water can still evaporate as clusters.⁵³ On the other hand, the micropores in the CFs had widths from 0.58 to 1.2 nm, which could only accommodate two to four water molecules in their cross sections. As a result, the hydrogen-bond network is effectively destroyed, and the cluster evaporation mechanism diminishes. In addition, water transport is hindered due to the small size of micropores, as well as the hydrophilic nature of the pore walls. Thus, the value of H_{vap} of the CFs is greater than that of the mesopore-containing PCFs. Because of the decreased water transport, the lower surface area, and the suppression of cluster evaporation mechanism, the CFs exhibited limited desalination performance.

Nano-confinement causes a disruption in the continuous hydrogen-bonding network, which plays an important role in the physical properties of water. For example, previous studies showed that nano-confinement could produce water in a variety of bonding states (*e.g.*, network water, intermediate water, and multimer water) with differing vaporization enthalpy.⁴⁵ As expected, it requires less energy to vaporize small water clusters collectively than to break each hydrogen bond and vaporize each water molecule individually.⁵⁴

In addition to the nano-confinement effects, the hierarchical porous structure of the PCFs provides an important factor for continuous desalination. Vaporization of water in porous media follows two stages. In the first stage, water flows from the bulk into the pores through capillary actions, and in the second stage, water evaporates and the air-water interface recedes on the pore surface.⁵⁵ The air-water interface is vital for water evaporation.⁵⁶ The vapor phase above the receding air-water interface quickly saturates, resulting in a concentration gradient of water vapor towards the bulk air. The concentration gradient becomes the driving force for water vapor molecules to escape the porous network and enter air.⁵⁷ In both stages, the pore tortuosity,

geometry, and size distribution affect water transport, as well as evaporation rates and efficiency.⁵⁸ The transport of water vapor from micropores to mesopores and then to macropores provide a “capillary valve effect” further facilitating vapor release and water evaporation. The slightly hydrophilic nature of the PCFs, combined with the capillary pressure in the hierarchical pores, allows a continuous film to develop, thus increasing the air-water interfacial area and leading to high desalination rates.⁵⁹

4.4 Experimental Section

Methyl methacrylate (MMA, $\geq 99\%$), acrylonitrile (AN, $\geq 99\%$), 2,2'-azobis(2-methylpropionitrile) (AIBN $\geq 98\%$), benzene ($\geq 99\%$), aluminium oxide (activated, neutral, Brockmann Activity I), *N,N*-dimethylformamide (DMF, $\geq 99.7\%$), and dimethyl sulfoxide (DMSO, $\geq 99.9\%$) were purchased from Sigma-Aldrich. Cumyl dithiobenzoate (CDB) was synthesized via a previously reported pathway.⁴³ Pumped methanol was used for polymer precipitation. MMA and AN were purified by alumina column filtration to remove inhibitors.

Synthesis and fabrication of carbon fibers. Poly(methyl methacrylate)-*block*-poly(acrylonitrile) (PMMA-*b*-PAN) was synthesized via reversible addition-fragmentation chain transfer (RAFT) polymerization according to a previous report with modifications.⁴⁵ First, a mixture of MMA (70.0 mL, 618 mmol), CDB (168.6 mg, 0.318 mmol), and AIBN (50.8 mg, 0.310 mmol) were dissolved in benzene (110 mL) in a 500-mL Schlenk flask. The solution was subjected to three cycles of freeze-pump-thaw (FPT) followed by back-filling with N₂ to remove dissolved oxygen gas. The reaction proceeded at 60 °C resulting in a PMMA macro-chain transfer agent (CTA). Three macro-CTAs were synthesized by polymerization at 60 °C for 14, 22, and 52 h, resulting in PMMA-C (41 kDa), PMMA-B (59 kDa), and PMMA-A (108 kDa), respectively (Figure S4.1). The PMMA macro-CTAs were precipitated in methanol, filtered, and dried under vacuum for 12 h.

The purified PMMA macro-CTAs were then used to synthesize PMMA-*b*-PAN block copolymers (BCP). The macro-CTAs were subject to the same molar ratios. The synthesis of BCP-B will serve as an example. BCP-B was synthesized by the mixture of PMMA-B macro-CTA (6.50 g, 110.1 μ mol), AN (26.0 mL, 433.1 mmol), AIBN (4.4 mg, 27.0 μ mol), and DMSO (72.2 mL). Note for both BCP-A, and BCP-C the molar ratios are the exact same. The AIBN was added last to the mixture immediately preceding the three FPT cycles. The mixture was then heated in an oil

bath at 65 °C under N₂ atmosphere for 8 h which resulted in precursors with PAN number-average molecular weights: BCP-B (36 kDa). Note the same molar ratios were used for PMMA-A, and PMMA-C however the reactions proceeded for 10 h (PMMA-A), and 12 h (PMMA-C) resulting in PAN molecular weights BCP-A (44 kDa), and BCP-C (66 kDa). The PMMA-*b*-PAN block copolymers were purified following the same steps as the PMMA macro-CTAs. The PAN homopolymer was synthesized with radical polymerization in a 250 mL Schlenk flask by adding AN (34.6 mL, 528 mmol), AIBN (15.08 mg, 91.83 mmol), *S,S*-dibenzyl trithiocarbonate (SSDT, 96.8 mg, 0.334 mmol), and DMSO (80 mL) into the mixture. The solution was subjected to three cycles of FPT and filled with N₂. The mixture was then heated at 60 °C for 12 h. The mixture was then diluted with 80 mL of DMF and then precipitated into MeOH. The precipitates were collected by filtration, washed with MeOH, and then dried in vacuo at 80 °C to remove the residual solvents.

The number-average molecular weights were measured with size exclusion chromatography (SEC) (EcoSEC HLC-8320GPC) equipped with a light scattering detector (DynaPro Nanostar photometer) (Table 4.2). The block copolymers were then dissolved in DMF (18 wt. %) overnight. The dissolved BCPs were electrospun at a flow rate of 0.020 mL min⁻¹ with 18 kV (using high power supply, Model P030HP1, Acopian Technical Company) and collected onto an aluminum drum with a spin rate of ~120 rpm. The as-spun fibers were oxidized at 280 °C with a heating rate of 1 °C min⁻¹ for 8 h under air to stabilize the fibers and then pyrolyzed at 800 °C for 1 h at a heating rate of 10 °C min⁻¹ in a tube furnace (Model STF55433C-1, Lindberg/Blue M) under N₂ atmosphere (N₂ flow rate, 200 standard cubic centimeters per minute).

Table 4.2. Characteristics of carbon fibers PCF-A, -B, -C, and CF and the precursor polymers

Fibers	Polymer precursor	Pore width (nm)	Surface area (m ² g ⁻¹) ^a	Pore volume (cm ³ g ⁻¹) ^b
CF	PAN	< 2	120	3.6
PCF-A	BCP-A	21.6	445	8.5
PCF-B	BCP-B	14.7	690	10.1
PCF-C	BCP-C	10.7	760	11.0

^a Values based on N₂ physisorption

^b Total pore volume of N₂ and CO₂ physisorption

Characterization. N₂ and CO₂ physisorption were performed at 77 and 273 K, respectively, using a 3Flex pore analyzer (Micrometric Instruments Company). Prior to physisorption, PCFs were degassed at 90 °C for 1 h and 300 °C for 10 h to remove any surface adsorbents. Pore width distributions were calculated using non-local density functional theory (NLDFT). Light absorption spectra were acquired using a UV-Vis-NIR spectrophotometer (Agilent Cary 5000). The ion concentrations were tracked with an inductively coupled plasma mass spectrometer (Agilent 7900 ICP-MS). A field-emission scanning electron microscope (FE-SEM, LEO 1550) was utilized to image the carbon fibers. An acceleration voltage of 2 kV and a working distance of ~3 mm were used. The SEM images were then processed using the ImageJ software. Differential scanning calorimetry (DSC) was performed between room temperature and 120 °C at a heating rate of 10 °C min⁻¹ under a N₂ stream (50 mL min⁻¹) on a Discovery DSC2500 (TA Instruments). The DSC was calibrated using indium [melting point (m.p.) = 156.60 °C] and zinc (m.p. = 419.47 °C) standards. The boiling point was measured as the midpoint of the endothermic peak.

Evaporation performance testing. Water evaporation experiments were conducted using a solar simulator (Newport 3M) with an output power of 1000 W m⁻² (1 sun irradiation) in a dark room. A power meter (Newport ORIEL Sol3A) controlled the output of the solar simulator. Each solar desalination sample was tested in Petri dishes along with a blank water sample as a control. The carbon fiber bundles were placed in a small cork support to ensure that they floated at the water-air interface. The mass loss of water was monitored using an analytical balance with a 0.01 mg resolution. Water vapor was condensed along a glass dome. Salt concentrations were measured with ICP-MS to track common ions within saltwater (Na⁺, Mg²⁺, K⁺, Ca²⁺) before and after desalination. Energy efficiency (η) for solar to vapor generation was calculated according to the following equation:

$$\eta = (mH_{\text{vap}})/(C_{\text{opt}} P_0) \quad (4.2)$$

where m is the mass flux, H_{vap} is the vaporization enthalpy of water, C_{opt} is the optical concentration on the absorber surface, and P_0 is the solar irradiation of 1 sun (1000 W m⁻²). The desalination rates were normalized to geometric surface area of each fiber mat exposed to the solar irradiation. Exposed area was calculated by measuring the sides and top of the carbon fiber mats above the floating material (cork).

4.5 Conclusions

In summary, block copolymer-based porous carbon fibers were demonstrated to be highly efficient materials for solar desalination. Importantly, the well-defined, interconnected and tunable, elucidated effects of mesopores and micropores on confined water evaporation enthalpy. The meso- and micro-porous carbon fibers showed strong light absorption of across the entire solar spectrum, thereby providing high photothermal energy conversion efficiency. The mesopore water confinement saw a reduced evaporation enthalpy more significantly than micropores, with desalination also varying with the pore size, surface area, and pore volume. In general, the enthalpy decreased as the mesopore size decreased. However, the enthalpy started to increase as the pore size was further reduced to the micropore range. Based on enthalpic estimations by DSC and dark-environment, in conjunction with prior simulation work, the smaller mesopores provide higher evaporation by lowering water density with broken hydrogen bonds. However, at even lower pore sizes (<2 nm) hydrogen bonds to both water molecules and carbon surfaces increase and lead to an increase in enthalpy for evaporation. The porous carbon fibers with a mesopore size of 10.7 nm were found to have the lowest water evaporation enthalpy and the highest desalination rate of $3.8 \text{ kg m}^{-2} \text{ h}^{-1}$ under one sun irradiation, which was hitherto unprecedented in the literature, for carbon based, single-stage solar desalination devices. In addition to high solar desalination rates, the porous carbon fibers exhibited excellent reusability and stability. Overall, this study highlighted the porosity as an achievable route to achieve high solar efficiency, high vaporization rate, and high sustainability. Based on these results, we expect porous materials including carbon fibers to hold great potentials for desalination, separation, filtration, and other environmental applications.

4.6 Supporting Information

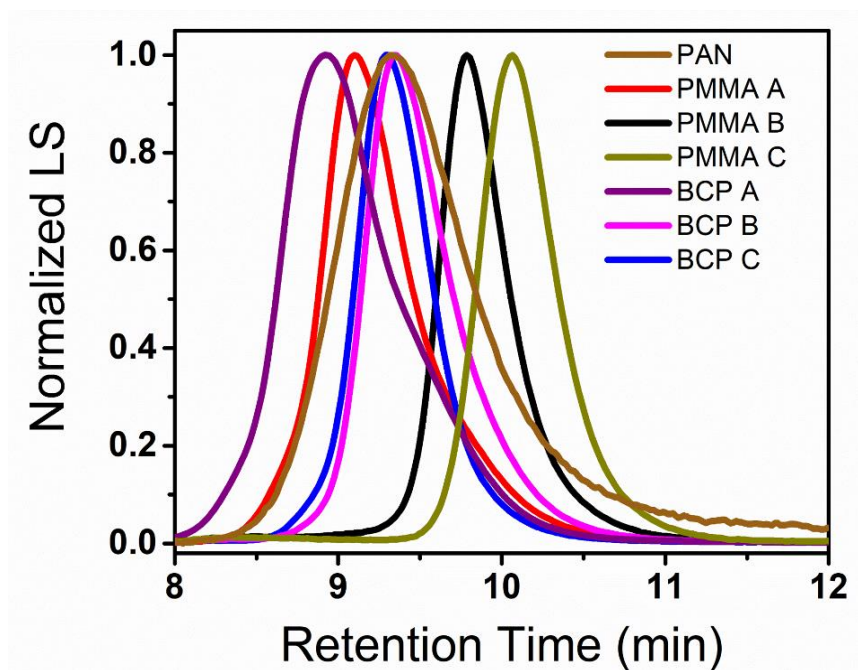


Figure S4.1. (a) Size exclusion chromatography (SEC) traces of PAN, PMMA, and the corresponding PMMA-*b*-PAN. The light scattering intensities were normalized for clarity.

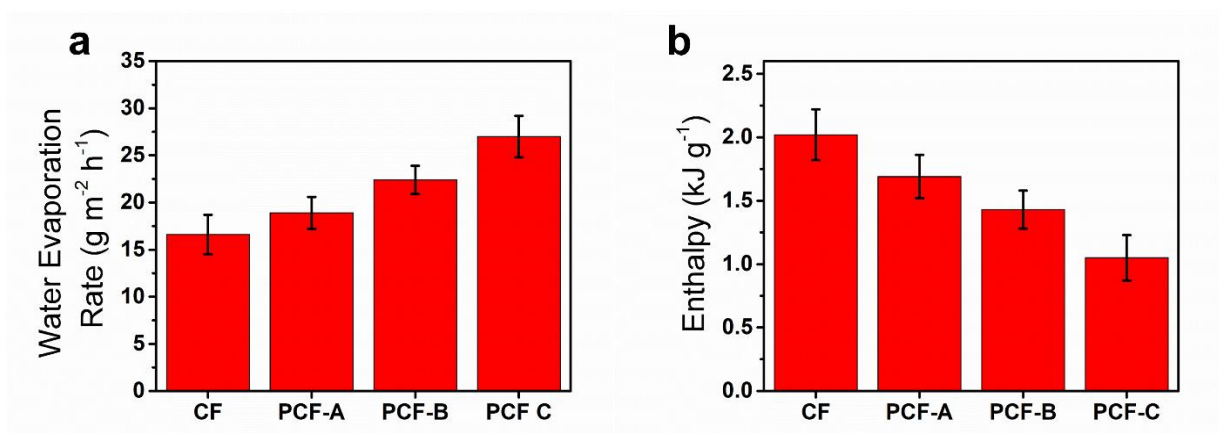


Figure S4.2. (a) Dark-environment (dark-field) evaporation rates of water using carbon fibers and porous carbon fibers. (b) Calculated equivalent enthalpy based on the water evaporation rate.

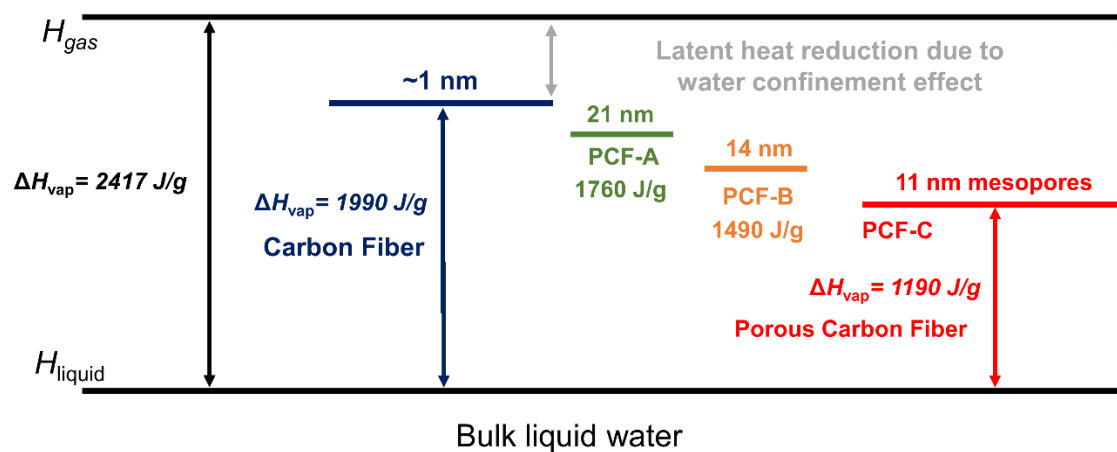


Figure S4.3. Scheme of water vaporization enthalpy reduction by the carbon fibers. All values are based on enthalpy measured by DSC. Water standardized enthalpy is based on standard temperature and pressure at 20 °C.

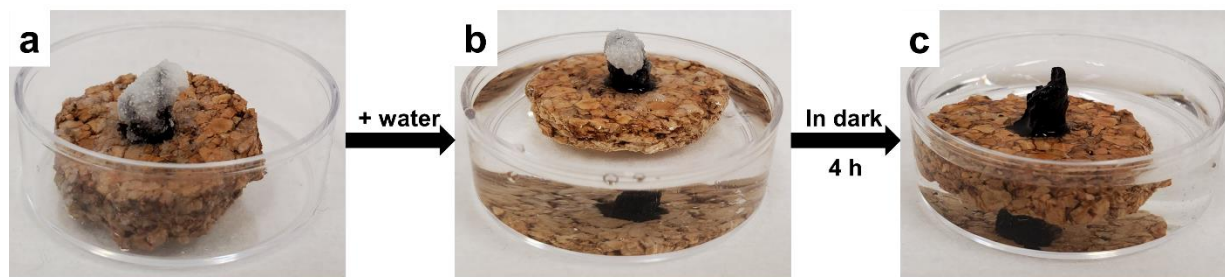


Figure S4.4. Self-cleaning capability of PCFs. (a) Salt built up if PCFs were not actively used. (b) Upon placement in saline water, the salt started dissolution. (c) The PCFs were placed in the dark represent self-cleaning at night. After 1 h, the salt was completely dissolved by water.

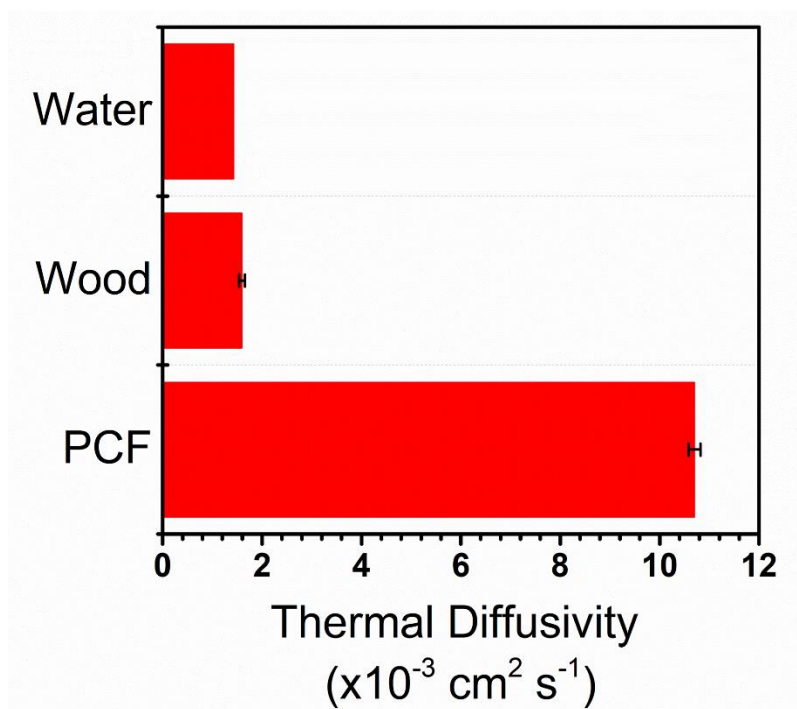


Figure S4.5. Thermal diffusivities of the floating material (wood), the porous carbon fibers, and water at standard temperature and pressure. For the wood (cork) material and the PCF, measurements from 3 samples measured each 3 times were conducted.

Table S4.1. Characteristics of the polymer precursors for PCF-A, B, C and CF along with the physisorption data of the carbon fibers.

Sample	PMMA M_n (kDa) ^a	PAN M_n (kDa) ^a	Total M_n (kDa) ^a	ϕ_{PAN}	Pore Width (nm)	Surface Area (N ₂) (m ² g ⁻¹)	Pore Volume (N ₂) (cm ³ g ⁻¹) ^b
PCF A	108	44	152	0.29	21.6	445	5.3
PCF B	59	36	95	0.37	14.7	690	6.6
PCF C	41	66	107	0.59	10.7	760	8.0
CF	-	46	46	1	< 2	120	~0

^a Calculated using size exclusion chromatography – light scattering detector

^b Volume based on N₂ physisorption only.

Table S4.2. DSC scans with PCF A, B, and C showing the average of 5 samples for each fiber set with weight and calculated enthalpy (H_{vap}) requirements.

Sample	PCF weight (mg)	H ₂ O weight (mg)	Water Abs (cm ³ g ⁻¹) ^a	H_{vap} DSC (J g ⁻¹) ^b	H_{vap} @ STP required (J) ^c	Calculated H_{vap} (J) ^d	% H_{vap} reduced @ STP ^e
PCF A	0.63	6.75	10.7	1760	165	119	28
PCF B	0.70	7.71	11.0	1600	188	123	34
PCF C	0.73	6.81	9.3	1380	166	94	43

^a Amount of water absorbed within the PCFs during DSC scan

^b Integrated DSC scan estimation for total enthalpy input for evaporation

^c Enthalpy required for the water content to evaporate at 1 atm and 25°C

^d Based on DSC estimates, the calculated energy (J) input to fully evaporate water within the PCF sample

^e Estimated % reduction of enthalpy from standard (2440 J

4.7 Acknowledgments

We acknowledge the use of the nanoscale characterization and fabrication laboratory (NCFL) and chemistry facilities at Virginia Tech. We also acknowledge Yuqing Li for assistance with thermal diffusion testing of the carbon fibers, as well as the toxicology lab and McAlister Council-Troche for aid in preparing ICP samples.

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Chapter 5. Humidity Effects on Electrospun Block Copolymers for Flexible Electrodes

This chapter has been adapted from a manuscript currently in preparation by J. M. Serrano, Glenn A. Spiering, Zhen Xu, Zacary L. Croft, Ke Cao, Dong Guo, Robert B. Moore, and Guoliang Liu

5.1 Abstract

Growing demands in flexible electronics have stimulated rapid development in electrodes with multi-faceted attributes. Porous carbon fibers (PCF) provide a potential means to achieve simultaneously flexibility, durability, and energy density. High energy density often necessitates pores for large surface areas, but pores generally diminish mechanical properties. Here we electrospin poly(methyl methacrylate)-block-poly(acrylonitrile) (PMMA-*b*-PAN) with vapor-induced phase separation (VIPS) using relative humidity (R.H.) and examine the changes in polymer morphology and resulting PCF porosity and flexibility. The determining polymer morphology factors evolve from PMMA-*b*-PAN microphase separation at 40-50% R.H., to VIPS combined with microphase separation at 60-70% R.H., and to vapor-induced precipitation at 80-90% R.H.. The subsequent carbonized fibers show corresponding porosity, flexibility, and electrochemical properties. Because VIPS enables the polymer fibers to outwardly reorganize PAN and produce continuous graphitic structures, PCF prepared from polymer fibers electrospun at 70% R.H. develop a mesoporous core and long-range graphitic carbon sheath. Owing to the core-sheath structure, these PCF exhibit flexibility and mechanical strength to withstand repeated bending while retaining a $249 \pm 20 \text{ F g}^{-1}$ capacitance. This work highlights the potential for

controlling block copolymer morphologies by processing conditions and PCF properties, providing a platform for designing flexible PCF for energy and environmental sciences.

5.2 Introduction

Next generation electronics demand structural electrodes that have combined high power density, energy density, flexibility, durability, and safety.¹ Structural electrode materials integrating all these properties are limited.^{2, 3} Fiber-based electrodes can potentially address structural electronic needs owing to their versatile functionality, flexibility, and strength.⁴ Several fiber-based materials have been studied including metal wires,⁵ metal composite fibers,⁶ conductive polymer fibers,⁷ and carbon fibers.⁸⁻¹⁰ Traditional metal wires are highly conductive but lack large surface area to provide high energy density.¹¹ Metal composite fibers are attractive for their conductivity and multifunctionality (piezoelectrics, nanogenerators, *etc.*), however their architectures are susceptible to tears and cracks.^{12, 13} Conductive polymer fibers (*e.g.*, polyaniline (PANI),⁷ poly(3,4-ethylenedioxythiophene) (PEDOT),¹⁴ and polypyrrole (PPy)¹⁵) possess good processability and can be easily integrated with other materials such as cobalt oxide wires,¹⁶ graphene oxide,¹⁷ and polymer binders.¹⁸ But swelling and shrinking of the conductive polymer fibers cause short electrode life.^{19, 20} Carbon fibers are known for their superior mechanical strength and have high conductivity similar to metal wires and high redox stability.²¹ Therefore, development of carbon fiber electrode is desirable for high-performance flexible electrodes.

State-of-the-art carbon fiber electrodes focus on enhancing energy density without compromising the mechanical properties such as flexibility. Enhanced energy density is often achieved with additives/dopants such as nanoparticles,²² composite layers,²³ and metal oxides.²⁴ However, pristine carbon fibers have low surface loading of additives/dopants and reduced

capacitance due to their small surface areas and porosity.^{25, 26} Even with exfoliation techniques, surface areas of carbon fibers remain low (typical surface areas of pristine fibers are $\sim 6 \text{ m}^2 \text{ g}^{-1}$ and exfoliated carbon fibers $\sim 92 \text{ m}^2 \text{ g}^{-1}$).²⁷ Porous carbon fibers potentially address the issue of low surface area but they often have reduced mechanical strength.²⁸ Adding metal wire components ameliorates the strength of porous carbon fibers, but detrimentally increases weight and decreases specific surface area. Therefore, a direct approach to developing porous carbon fiber (PCF) that retains mechanical properties (particularly tensile strength and toughness) would allow enhanced energy density and flexibility.

Polyacrylonitrile (PAN)-derived carbon fibers possess intrinsic strength from long-range graphitic carbon, but certain pore fabrication methods can disrupt the graphitic structure. For example, PAN blended with sacrificial polymers such as poly(styrene) (PS)²⁹ and poly (methyl methacrylate) (PMMA)³⁰ lead to broad pore/graphitic carbon distribution during carbonization. Whereas, PAN-based copolymers reach even higher porosity and surface area with narrow pore/graphitic carbon distribution in resulting PCF.^{31, 32} The high degree of porosity and narrow pore distributions might disrupt long-range graphitic structures and compromise the mechanical properties.³³⁻³⁵ Alternatively vapor induced phase separation (VIPS)³⁶ generates polymer-derived porous separation membranes which retain excellent mechanical strength.³⁷ VIPS in membranes show tunable crystalline morphology which enhances long-range crystallinity and subsequent mechanical properties.³⁸ However, VIPS effects on PAN-derived carbon fibers has limited studies in resulting electrochemical and mechanical properties.^{39, 40} Therefore, the potential synergistic effects on pore generation with retained long-range graphitic structures are unknown.

Recently our laboratory has developed PCF from poly(methyl methacrylate)-*block*-poly(acrylonitrile) (PMMA-*b*-PAN).³² These PCF have shown outstanding capabilities for energy

storage; however, the mechanical properties remain to be elucidated.⁴¹ Typically, the electrospun block copolymers develop microphase separation and subsequent narrowly dispersed mesopores in the carbon fibers.³² The block copolymer microphase separation in conjunction with VIPS has hitherto been unknown.⁴²⁻⁵⁰ Herein we study the morphologies of electrospun PMMA-*b*-PAN fibers in relative humidity (R.H.) of 40 to 90% to investigate synergistic microphase separation and VIPS (Figure 5.1). Water vapor acts as a non-solvent to induce polymer reorganization in the electrospun fibers. The reorganization develops different PMMA and PAN structures directly influencing the PCF physical, mechanical, and electrochemical properties. At lower humidity (40-50%) the polymer fibers mainly undergo block copolymer microphase separation which develops into uniform mesopores. At mid-range humidity (60-70%) the polymer fibers show reorganization of PAN towards to sheath and PMMA to the core which results in a carbon sheath and larger internal pores. At high humidity (80-90%) the polymer fibers develop beads and clumps during electrospinning due to nonsolvent vapor-induced precipitation. By systematically studying the effect of humidity on the block copolymer fiber morphology, we highlight the tunability of PCF properties for use as flexible electrode.

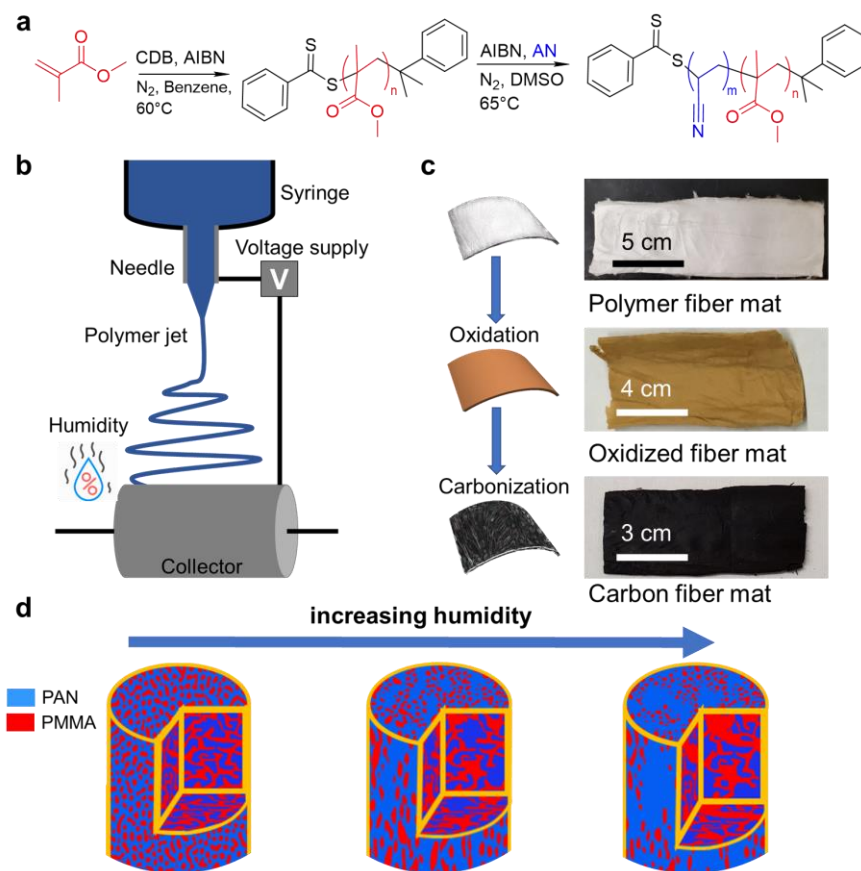


Figure 5.1. (a) PMMA-*b*-PAN was synthesized *via* controlled radical polymerization, (cumyl dithiobenzoate (CDB), azobisisobutyronitrile (AIBN), acrylonitrile (AN), dimethyl sulfoxide (DMSO)). (b) PMMA-*b*-PAN was electrospun into fiber mats under conditions of varying humidity. (c) PMMA-*b*-PAN fiber mats were oxidized at 280 °C and subsequently carbonized at 800 °C. The photographs show representative fiber mats after each step. (d) Due to the presence of non-solvent water vapor, upon increasing humidity the determining factors of PMMA-*b*-PAN morphologies evolve from block copolymer microphase separation, to VIPS, and to vapor induced precipitation.

5.3 Experimental Section

Chemicals. Methyl methacrylate (MMA, $\geq 99\%$), acrylonitrile (AN, $\geq 99\%$), azobisisobutyronitrile (AIBN, $\geq 98\%$), benzene ($\geq 99\%$), aluminum oxide (activated, neutral, Brockmann Activity I), *N,N*-dimethylformamide (DMF, $\geq 99.7\%$), and dimethyl sulfoxide (DMSO, $\geq 99.9\%$) were purchased from Sigma-Aldrich. Cumyl dithiobenzoate (CDB) was synthesized *via* a previously reported protocol.²⁰ Methanol (Pharmco-AAPER) was used for polymer precipitation. Nickel foam (MTI Corporation) was used as electrode substrates. Inhibitors in MMA and AN were removed by alumina columns; all other chemicals were used as received.

Preparation of PCF. PMMA-*b*-PAN was synthesized *via* reversible addition-fragmentation chain transfer (RAFT) polymerization modified from a previous report.⁵¹ First, MMA (70.0 mL, 618 mmol), CDB (169 mg, 0.318 mmol), and AIBN (50.8 mg, 0.310 mmol) were dissolved in benzene (120 mL) in a 1-L Schlenk flask. The mixture was subjected to four cycles of freeze-pump-thaw (FPT) followed by back-filling with N₂ to remove dissolved oxygen. The reaction proceeded at 60 °C for 27 h, resulting in a PMMA macro-chain transfer agent (macro-CTA). The macro-CTA was precipitated in methanol, filtered, and dried in air for 24 h. The purified macro-CTA (65.0 g, 1.08 mmol) was then mixed with AN (260 mL, 4.33 mol), AIBN (4.40 mg, 270 μ mol), and DMSO (700 mL) into a 2-L Schlenk flask to synthesize PMMA-*b*-PAN. The mixture was degassed by four FPT cycles and then heated in an oil bath at 65 °C under an N₂ atmosphere for 24 h. The resulting PMMA-*b*-PAN block copolymers were purified following the same steps as those of PMMA macro-CTA. The number average molecular weights (M_n) and polydispersity index (PDI) were measured with size exclusion chromatography (SEC) (EcoSEC HLC-8320GPC) equipped with a light scattering detector (DynaPro Nanostar photometer).

PMMA-*b*-PAN ($M_n = 171$ kDa, PDI = 1.11) (Figure S5.1) was dissolved in DMF at a concentration of 17 wt.%. The dissolved PMMA-*b*-PAN was electrospun at an injection rate of $0.020 \text{ mL min}^{-1}$ and a voltage bias of 18 kV provided by a high-voltage supply (Model P030HP1, Acopian Technical Company). Electrospun fibers were collected by an aluminum drum with a rotating speed of ~ 280 rotations per minute (rpm). The entire apparatus was placed within a transparent epoxy chamber equipped with a humidifier and a hygrometer to tune humidity during electrospinning. Relative humidity (R.H.) to room temperature (~ 23 °C) was set to 40, 50, 60, 70, 80, and 90% with a $\pm 3\%$ tolerance to electrospin six sets of polymer fiber mats. The subsequent oxidized and carbonized fibers were designated as oxidized or PCF with their corresponding polymer fiber R.H. treatment throughout the paper.

The as-spun fibers were oxidized and stabilized at 280 °C for 8 h in air and then pyrolyzed at 800 °C for 1 h in an electrical tube furnace (Model STF55433C-1, Lindberg/Blue M) with a constant flow of N_2 at 200 standard cubic centimeters per minute (sccm). The resultant PCF was used without further activation.

Material Characterizations. The fibers were imaged with a scanning electron microscope (LEO Zeiss 1550 SEM, acceleration voltage: 2 - 4 kV, working distance: ~ 3 mm). Because of inadequate electrical conductivity, the as-spun and oxidized fibers were coated with ~ 4 nm iridium prior to SEM imaging. N_2 and CO_2 physisorptions were conducted at 77 K and 273 K, respectively, on a 3Flex Pore Analyzer (Micrometric Instruments Company). Prior to physisorption, PCF was degassed at 90 °C for 1 h and 300 °C for 10 h to remove any potential adsorbents on the carbon surfaces. Surface areas were calculated based on Brunauer-Emmett-Teller (BET) theory. Pore size distributions were obtained using non-localized density functional theory (NLDFT), similar to previous reports.²¹ The mechanical properties were evaluated based on the cross-sectional area of

the fiber mats which were placed under tension. The fibers were tested with dynamic mechanical analysis (DMA) with fiber mats in the tensile mode. Calipers with ± 0.01 mm were used to measure cross-sectional area, but SEM images were also taken to verify PCF fiber mat dimensions for DMA (Figure S5.9).

Electrochemical Characterizations. All electrochemical tests were performed on a PARSTAT 4000+ electrochemical workstation (Princeton Applied Research, AMETEK Inc.) with a three-electrode testing configuration. PCF (~ 2 -3 mg) was placed between two pieces of nickel foam ($\sim 1 \times 3$ cm²) so that only the top portion of the PCF was in contact with the nickel foam. The electrodes were then pressed at 4 metric tons using a benchtop hydraulic shop press (Stongway, Model 46269). The actual mass loading of PCF was measured using an analytical balance (Model Mettler Toledo XSE105) with a sensitivity of ± 0.01 mg. The mass was checked before and after pressing to account for any material loss during the pressing process.

The PCF electrodes were then tested using cyclic voltammetry (CV) to evaluate the electrochemical performance. An Ag/AgCl electrode (in saturated KCl aqueous solution) and a piece of nickel foam were used as the reference and counter electrodes, respectively. The electrolyte was 3 M KOH solution for electrochemical tests. CV curves were collected within a potential window from 0 to -0.8 V vs. Ag/AgCl at various scan rates between 10 and 1000 mV s⁻¹. The PCF gravimetric capacitances from CV were calculated using the following equation,⁵²

$$C = \frac{1}{2(V_t - V_0)v} \int_{V_0}^{V_t} |I_m(V)| dV \quad (5.1)$$

where $I_m(V)$ is the current density (A g⁻¹); v is the scan rate (mV s⁻¹); V_0 and V_t are the lower and upper potential limits of the potential window, respectively. For the flexible supercapacitors a quasi-solid-state electrode was created with PCF electrodes and a PVA/KOH electrolyte. A solution of PVA ($M_w \sim 35$ kDa) and deionized water (1:2 wt. ratio) was mixed for 2 h in a flask at

80 °C. Once the solution appeared homogeneous, 10 mL of 6 M KOH solution was added and mixed for 15 min. The solution was then poured into a glass petri dish which contained two symmetric PCF electrodes. Once the electrodes were fully submerged, the petri dish containing PCF-electrodes and PVA/KOH was placed in a freezer for 2 h. The subsequent quasi-solid-state gel electrode was then tested with CV with a two-electrode setup from 0 to 1.1 V at scan rates of 10-1000 mV s⁻¹. The gravimetric capacitance was calculated with eq. 5.1.

USAXS/SAXS Characterization. Ultra-small-angle X-ray scattering (USAXS)/small-angle X-ray scattering (SAXS) measurements were collected at beamline 9-ID-C at the Advanced Photon Source (APS) at Argonne National Laboratory (Lemont, Illinois).⁵³ Samples were mounted between two pieces of 3M Scotch tape. The X-ray energy was 21 keV, and the X-ray wavelength was 0.5904 Å. Data were acquired over 90 s for USAXS and 20 s for SAXS. The beam size was 0.8 mm x 0.8 mm for USAXS and 0.8 mm x 0.2 mm for SAXS. Data were reduced and corrected for background, thickness, and transmission using the Indra⁵⁴ and Nika⁵⁵ programs for Igor Pro. The data were output on an absolute scale. The Irena program for Igor Pro was used to merge same-specimen USAXS and SAXS profiles,⁵⁴ yielding a continuous scattering vector (q) range from 0.001 to about 16 nm⁻¹. Scattering plots are presented as scattering intensity, $I(q)$, versus scattering vector q , where $q = (4\pi/\lambda)\sin(\theta)$, θ is one half of the scattering angle and λ is the X-ray wavelength. Slit-smeared USAXS data were desmeared using Indra, yielding pinhole equivalent data. Merged USAXS/SAXS profiles were fit to the Unified Fit⁵⁶ function using Irena.

Unified Fit. The Unified Fit function⁵⁶ is used to fit multiple populations of scatterers each with a Guinier knee and a power law decay. A single level can be expressed as:

$$I_i(q) = G_i e^{-\frac{q^2 R_{g,i}^2}{3}} + e^{-\frac{q^2 R_{gco,i}^2}{3}} B_i \left\{ \frac{\left(\text{erf}\left(\frac{k q R_{g,i}}{\sqrt{6}} \right) \right)^3}{q} \right\}^{P_i} \quad (5.2)$$

where q is the scattering vector, $I_i(q)$ is the intensity of the i th level as a function of q , G_i is the Guinier prefactor, $R_{g,i}$ is the radius of gyration of the scatterer, B_i is the power-law prefactor, erf is the error function, and P_i is the Porod exponent. $R_{gco,i}$ is high q cutoff for the power-law, typically equal to $R_{g(i-1)}$. The term k is 1 for surface fractals and 1.06 for mass fractals. Many levels are summed as:

$$I(q) = \sum_{i=1}^N \left[G_i e^{-\frac{q^2 R_{g,i}^2}{3}} + e^{-\frac{q^2 R_{gco,i}^2}{3}} B_i \left\{ \frac{\left(erf\left(\frac{q R_{g,i}}{\sqrt{6}}\right) \right)^3}{q} \right\}^{P_i} \right] \quad (5.3)$$

The Unified Fit can be modified to accommodate for a weak structure factor. The Born-Green closure of the Ornstein-Zernike equation is used to modify the scattering pattern:⁵⁷

$$S(q) = \frac{1}{1+p*\theta(q,\eta)} \quad (5.4)$$

where $S(q)$ is the structure factor, p is the packing factor, and $\theta(q,\eta)$ is the spherical amplitude function,

$$\theta(q,\eta) = 3 \frac{\sin(q\eta) - q\eta \cos(q\eta)}{(q\eta)^3} \quad (5.5)$$

where η is the radial correlation distance. $S(q)$ is multiplied to $I_i(q)$ to include structure factor contributions to the desired level in the Unified Fit function.

5.4 Results & Discussion

Electrospinning and Fiber Morphology. Block copolymer derived porous carbon fibers showed a high degree of control over the pore structure, surface area, and electrochemical properties.³² In our previous reports,^{51, 52, 58} electrospun PMMA-*b*-PAN fibers exhibited kinetically trapped microphase separation of PMMA and PAN domains. The polymer morphology carried over to the resulting porous carbon fibers, but the effects of solvent/non-solvent on block copolymer phase

separation in fibers has not been fully elucidated. In addition, the morphological structures require further investigation in the electrospun polymer fibers, oxidized fibers, and carbon fibers.

Humidity serves as a non-solvent vapor that directly influences the morphology and domain size in block copolymer fibers. Here the PMMA-*b*-PAN fibers were subject to various electrospinning conditions under 40-90% R.H.. The electrospun polymer fibers, oxidized fibers, and carbon fibers are designated by the humidity levels during electrospinning. The 40%-polymer fibers showed well-dispersed domains (Figure 5.2a). The fiber skin appeared slightly smeared after the electrospinning flight. The 40% and 50% polymer fibers shared similar morphologies in the cross section with microphase separation of PMMA and PAN (Figure 2a, b). The 60% polymer fibers exhibited PAN sheath development on the fiber surface (Figure 5.2c). The 70% polymer fibers also showed a PAN sheath layer, and the microphase separation was still visible in the cross section (Figure 5.2d). Lastly, the 80% and 90% polymer fibers showed tantamount PAN sheath development. In addition, larger pores appeared inside the polymer fibers possibly due to an effect of non-solvent induced phase precipitation.^{59, 60}

The humidity also affected the structure of the fibers with regards to fiber alignment. At a low drum-rotation rate of ~ 280 rpm, the fibers lacked significant alignment but were still marginally aligned in the axial direction owing to the drum-shape fiber collector. The 40-70% polymer fibers retained the individual fiber shape and these fibers more or less shared similar fiber alignment (Figure 2S). However, the 80-90% polymer fibers showed a different structure with much less axial alignment. The adjacent fibers tended to fuse, either intersectionally or parallelly (Figure 2S e, f).

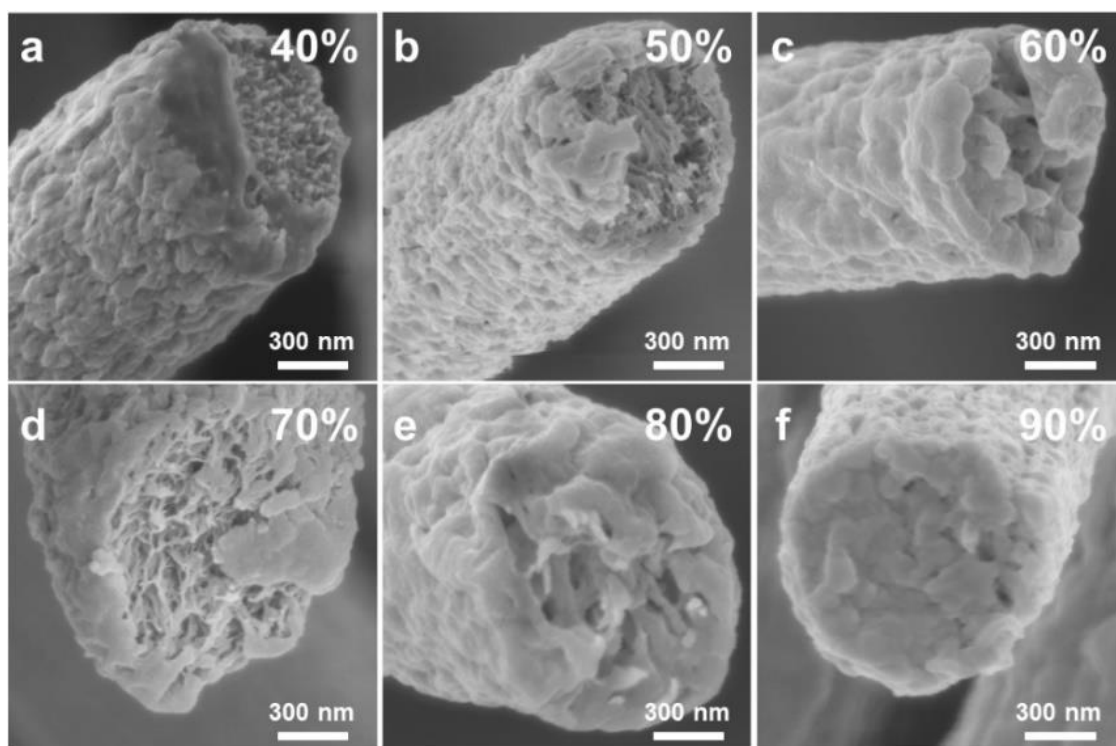


Figure 5.2. Representative SEM images of PMMA-*b*-PAN fibers immediately after electrospinning under conditions of (a) 40%, (b) 50%, (c) 60%, (d) 70%, (e) 80%, and (f) 90% R.H..

The block copolymer phase separation is of paramount importance for the physical, mechanical, and electrochemical properties of the resulting PCF. Typically, lower humidity levels barely affected the solvent evaporation and thus the fibers exhibited kinetically trapped PAN and PMMA domains,⁶¹ similar to the electrospun PMMA-*b*-PAN fibers in our previous reports.^{32, 58} The higher humidity levels, however, induced a non-solvent effect on the polymer jets and disrupted the block copolymer microphase separation. Thus, the PMMA-*b*-PAN fibers possessed complex phase-separated structures arising from the combined effects of solvent evaporation, non-solvent induced phase separation, and block copolymer microphase separation. First, SEM displayed a trend of PAN reorganization towards the sheath and PMMA migration towards the core (Figure S5.2), possibly driven by the greater hydrophobicity^{62, 63} and surface energy⁶³ of PMMA than those of

PAN. Surface energies of PMMA and PAN are $\sim 41 \text{ mN m}^{-1}$ and $\sim 27 \text{ mN m}^{-1}$, respectively.⁶³ In addition, PAN domains were subject to electrostatic repulsion within the jet stream during electrospinning, and thus the PAN domains reorganized along the sheath of the fiber.^{64, 65} Furthermore, a “polymer precipitation” effect was visible in the 80-90% polymer fibers where polymer clumps formed because of the high humidity levels (Figure S5.3). The clump formation is a known complication in electrospinning that accompanies non-solvent vapor (*i.e.*, humidity).³¹ Lastly, the high humidity also reduces the speed at which the solvent (DMF) evaporates from the fibers, thereby providing the polymer chains with mobility to reorganize. The reorganization in high humidity allows PMMA-*b*-PAN to reach better microphase separation than the kinetically trapped morphologies in lower humidity.⁶¹

Oxidation provides stability for the polymer fibers prior to carbonization, but also changes the block copolymer domain size and microphase separation during reorganization.⁶⁶ Previous reports have shown that oxidation partially degrades PMMA into pores and partially cross-links PAN into a network structure.⁵⁸ The 40-50% oxidized fibers retained the PMMA and PAN domains derived from the polymer fibers, and both the skin surface and cross-section showed relatively uniform pores (Figure 5.3a, b). However, in 60% oxidized fibers, portions of the PMMA domains coalesced and developed into non-uniform pores with greater dispersity than at 40-50% oxidized fibers (Figure S5.4c). Portions of the PAN domains developed into ridges along the fiber sheath (Figure 5.3c). The 70% oxidized fibers showed the coalescence of PMMA escalated and the non-uniform pores were more prevalent in both the cross-section and skin surface (Figure 5.3d, Figure S5.4d). The pore non-uniformity was the most apparent in 80-90% oxidized fibers, as depicted by the large voids (Figure 5.3e, f). Zoomed-out view of the 80-90% oxidized fibers showed that they retained the fused structures from the as-spun fibers (Figure S5.5).

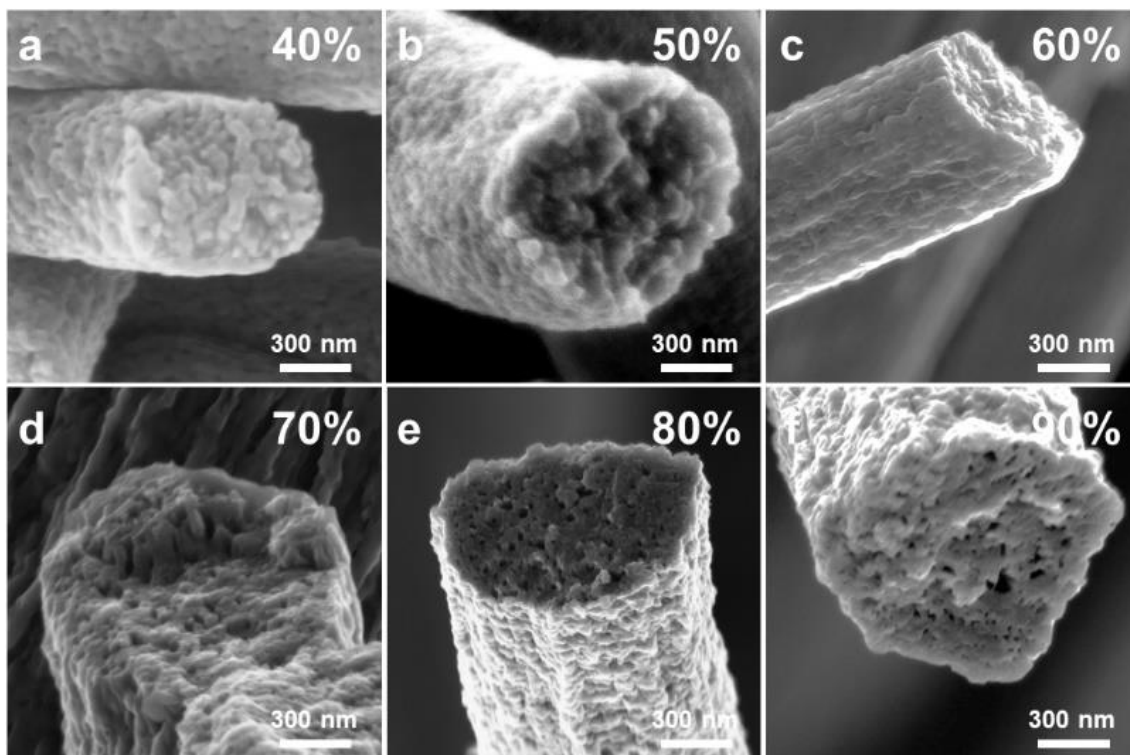


Figure 5.3. Representative SEM images of PMMA-*b*-PAN fibers after oxidization at 280 °C. The polymer fibers were electrospun under conditions of (a) 40%, (b) 50%, (c) 60%, (d) 70%, (e) 80%, and (f) 90% R.H..

Carbonization decomposes PMMA and completes the PAN cross-linking which solidifies the final morphology into a porous carbon network *via* pyrolysis. The 40-50% PCF resembled our previously reported PMMA-*b*-PAN-derived carbon fibers prepared under similar conditions.³⁵ These carbon fibers consisted of the typical porous structures templated by the PAN and PMMA domains that were kinetically trapped by electrospinning and PAN cross-linking (Figure 5.4a, b). The 60% PCF started to show a slight pore size difference along the exterior of the fibers (Figure 5.4c). Reaching a critical point of the non-solvent effect, the 70% PCF showed non-uniform pore sizes, as well as a carbon sheath layer due to the PAN sheath developed during electrospinning and oxidation (Figure 5.4d). We expect these fibers to be flexible because of a continuous layer of carbon sheath.⁶⁷ The non-solvent effect became more severe as the humidity level increased during

electrospinning. The 80% carbon fibers exhibited ridge-like carbon structures derived from PAN, leaving behind grooves on the fiber skin surface (Figure 5.4e). Similarly, the 90% PCF possessed non-uniform pore shapes in the cross-section arising from more non-solvent induced phase separation than low humidity fibers.^{68, 69}

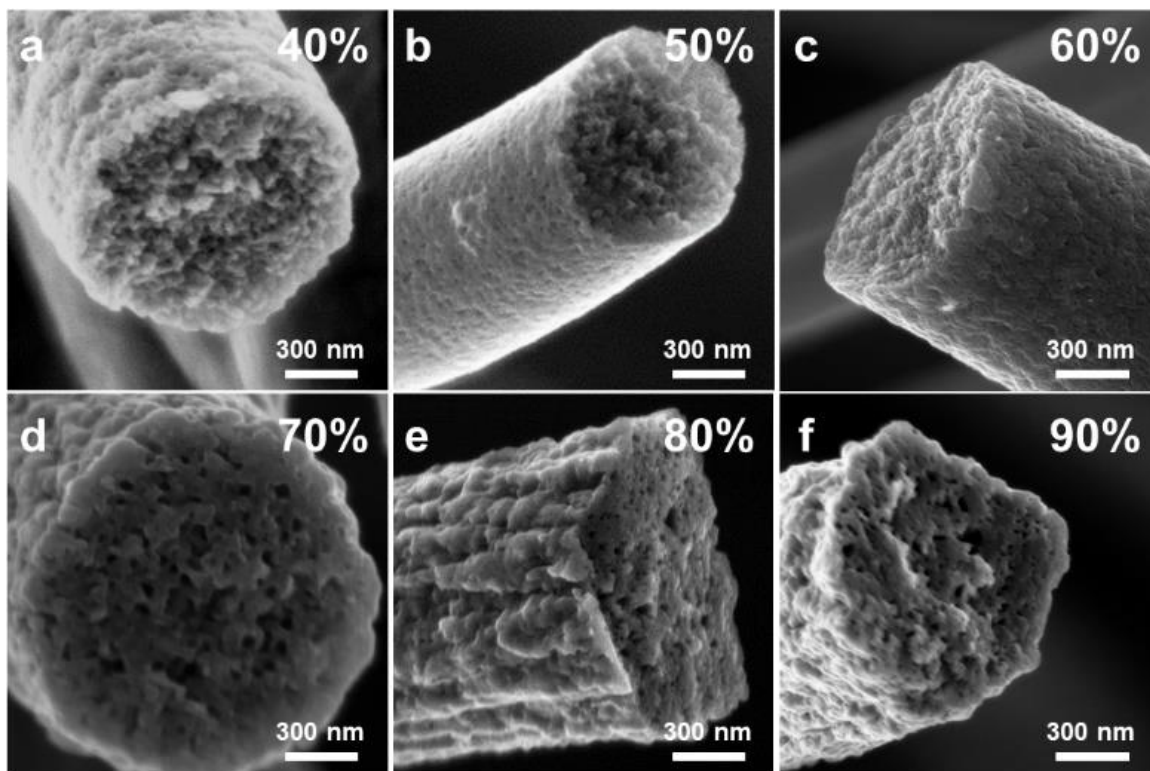


Figure 5.4. Representative SEM images of carbon fibers after oxidation of PMMA-*b*-PAN fibers at 280 °C and carbonization at 800 °C. The polymer fibers were electrospun under conditions of (a) 40%, (b) 50%, (c) 60%, (d) 70%, (e) 80%, and (f) 90% R.H..

The phase separation of block copolymer affects the physical properties of the fibers including pore size, surface area, and pore distribution. PMMA domains generate pores, but the coalescent PMMA domains increase the pore size, reduce the number of pores, and thus decrease the overall surface area. The PMMA domains tend to reorganize towards the fiber interior during high-

humidity electrospinning. The PAN sheath layer possibly fully encapsulates the pores inside the carbon fibers and make them inaccessible. The reorganization also induces the fibers to shift from a conventional cylindrical shape (40-60% humidity) to a non-uniform clumping shape with formation of beads (80-90% humidity) (Figure S5.6). Overall, SEM suggests a decreasing surface area, pore volume, and pore uniformity as the humidity level increases (Figure S5.7).

Physisorption properties of PCF. Physisorption revealed the pore size and surface areas of porous carbon fibers (PCF). N₂ isotherms of the PCF showed type IV characteristics (Figure 5.5), and CO₂ isotherms type I characteristics (Figure 5.6), as defined by the International Union of Pure and Applied Chemistry (IUPAC).⁷⁰ Based on the quantity of gas adsorbed and the hysteresis, N₂ isotherms provided insights into mesopore sizes (2 – 50 nm), mesopore volumes, and surface areas, whereas CO₂ isotherms provided information about the micropores (< 2 nm).

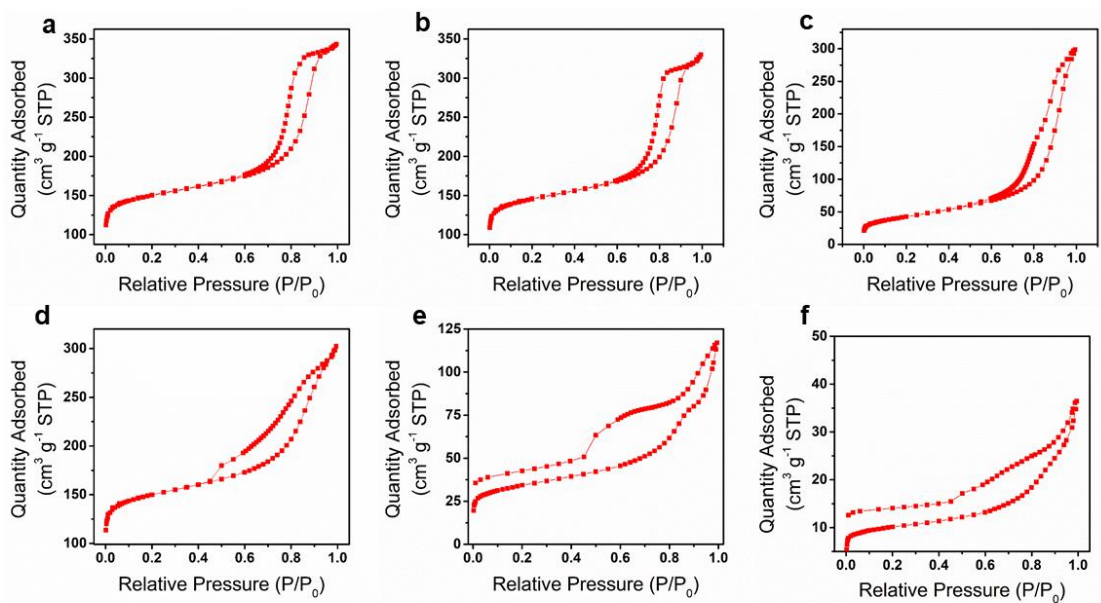


Figure 5.5. Physisorption data N₂ for carbonized fibers for (a) 40%, (b) 50%, (c) 60%, (d) 70%, (e) 80%, and (f) 90% R.H..

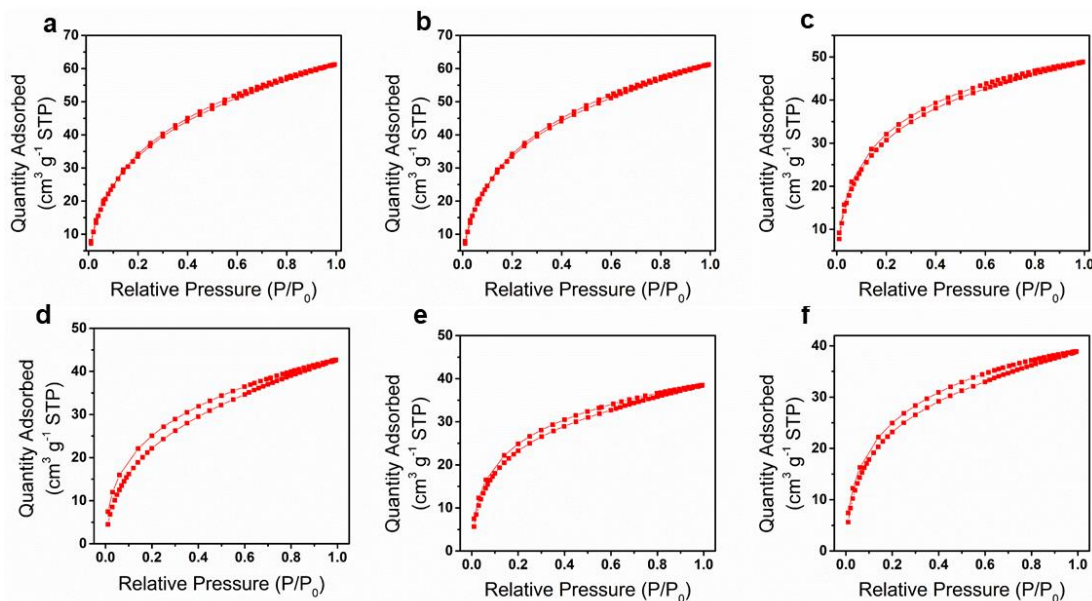


Figure 5.6. Physisorption data CO₂ for carbonized fibers for (a) 40%, (b) 50%, (c) 60%, (d) 70%, (e) 80%, and (f) 90% R.H..

By using non-linear density functional theory (NLDFT) on both N₂ and CO₂ physisorption, the pore width distributions were obtained (Figure 7).⁷⁰ The resulting porous carbon fibers contained various mesopore characteristics. The 40% PCF showed a clearly defined unimodal mesopore peak at ~ 14 nm (Figure 5.7). The 50% PCF displayed a similar unimodal peak centered at ~ 15 nm with similar pore volumes. At 60% R.H., the PCF mesopore size centered at ~ 17 nm and the pore size dispersity increased, as evidenced by the increasing full width at half maximum (FWHM). For the 70% PCF, the FWHM further increased, and a shoulder appeared at > 30 nm, but the mesopore size did not change drastically from the 60% PCF. The unimodal mesopore peak nearly disappeared at 80-90% humidity, and the population of mesopores > 20 nm notably increased. In addition, the overall pore volumes of 80% and 90% PCF drastically decreased (Figures 5.5 and 5.7 and Table 5.1). The micropores in all PCF were trimodal and centered about ~ 0.58, 0.86, and

1.2 nm (Figure 5.7). We attribute the micropores to missing graphitic networks within PAN derived carbon, which is present throughout all PCF and PAN-derived carbon fibers.⁵¹

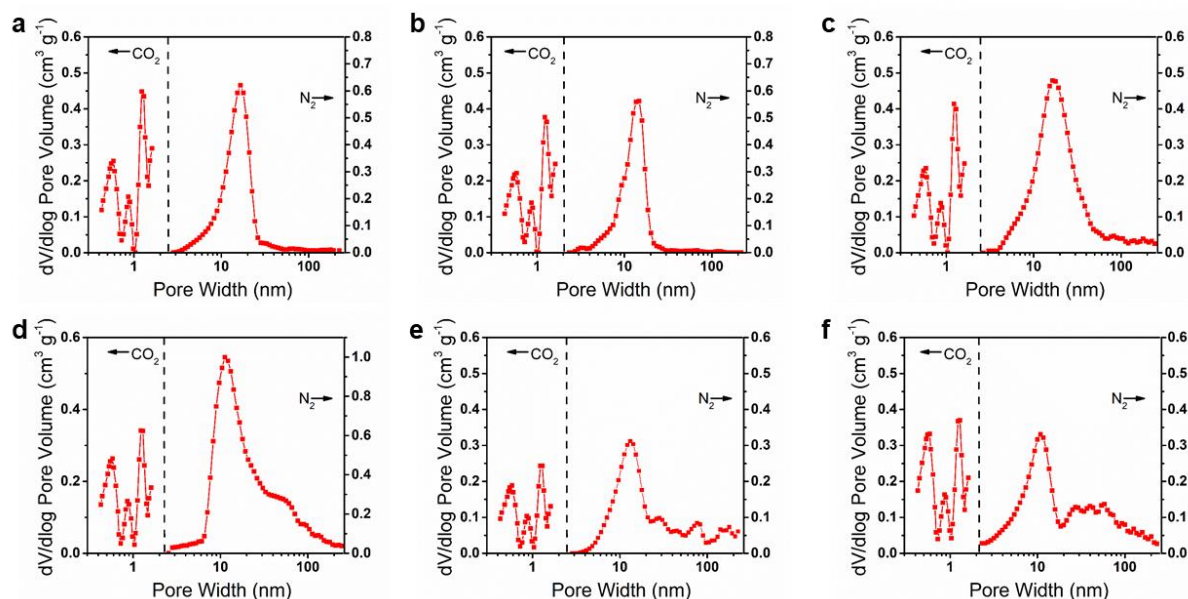


Figure 5.7. Pore width distributions of carbon fibers calculated using the NLDFT method, based on physisorption of N₂ for mesopores and CO₂ for micropores. The corresponding polymer fibers were electrospun under conditions of (a) 40%, (b) 50%, (c) 60%, (d) 70%, (e) 80%, and (f) 90% R.H..

The PCF surface area and pore width distributions reflected similar trends to the block copolymer morphology observations from SEM. The pore volume for 40% PCF was 0.487 cm³ g⁻¹. The pore volume increased with humidity up to 0.572 cm³ g⁻¹ (at 70% R.H.) then drastically decreased with humidity down to 0.053 cm³ g⁻¹ (at 90% R.H.) (Table 5.1). The coalescence of the PMMA domains was observed in the SEM images (for both the polymer and oxidized fibers) and confirmed by physisorption. The coalescent PMMA domains generated merged mesopores and reduced the overall pore volume. Moreover, at 80% and 90% R.H., the non-solvent induced phase separation became a dominant effect that further reduced the pore uniformity and pore volume.

Lastly, the PAN sheath created a carbon sheath, which also likely decreased the accessible internal pore volume.

Table 5.1. Surface area, pore volume, and peak mesopore size based on nitrogen physisorption data for 40-90% PCF.

R.H. (%)	Surface area (m ² g ⁻¹)	Pore volume (cm ³ g ⁻¹)	Peak pore size (nm)
40%	567	0.487	~14
50%	559	0.491	~15
60%	545	0.512	~17
70%	536	0.572	~16
80%	383	0.102	~13
90%	231	0.053	~12

USAXS/SAXS characterization of PCF. USAXS/SAXS investigated the morphological evolution of the electrospun mats. Merged USAXS/SAXS profiles for the spun fibers show two features (Figure 5.8a), a knee between 0.02 nm⁻¹ and 0.1 nm⁻¹, associated with phase separation between PAN and PMMA domains, and a knee between 0.002 nm⁻¹ and 0.02 nm⁻¹, associated with the diameter of the spun fiber. Notably, the oscillations associated with a low polydispersity are present for the fiber diameter feature spun at 60, 70, and 80% relative humidity. At 40% R.H., no phase separation occurs until DMF is quickly dissipated by electrostatic forces, resulting in PAN and PMMA being trapped in a relatively homogenous state. As R.H. increases from 50% to 80% R.H., the effects of vapor-induced phase separation increase. At 90% R.H., no phase separation is detected in SAXS. The copolymer may precipitate before regular phases develop. Since PAN is slightly more hydrophilic than PMMA, PAN orients towards the surfaces of high R.H. fibers, which may hinder further phase separation. The scattering profiles were fit to the Unified Fit function to extract radius of gyration of the phase separated feature (Figure 5.9). The radius of gyration of this feature decreased to a minimum of 39.2 nm at 70% R.H.. This R.H. may be the

proper balance of thermodynamic driving force relative to DMF evaporation rate to form a more thermodynamically favorable state.

The USAXS and SAXS profiles for oxidized fibers were combined (Figure 5.8b). A feature between 0.06 nm^{-1} and 0.3 nm^{-1} and a feature between 0.3 nm^{-1} and 1 nm^{-1} are observed in the scattering profiles for the oxidized fibers, in addition to the fiber diameter feature between 0.002 nm^{-1} and 0.02 nm^{-1} . Many concurrent processes, such as phase reorganization, PAN crosslinking, and degradation, occur during oxidation, making feature assignment challenging. The larger feature, between 0.06 nm^{-1} and 0.3 nm^{-1} , likely arises due to PMMA and PAN phase separation, and the smaller feature, between 0.3 nm^{-1} and 1 nm^{-1} , is likely due to the emergence of the pores. Interestingly, neither feature size trends strongly with relative humidity. At all relative humidity values, the phase separation features have a radius of gyration around 14 nm and the pore features have a radius of gyration of about 4 nm (Figure 5.9).

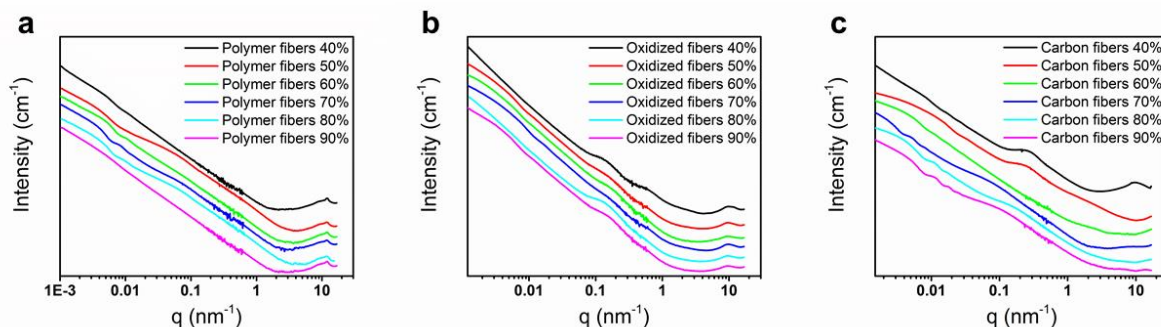


Figure 5.8. USAXS/SAXS profiles of (a) the as-spun block copolymer fiber mats under conditions of 40-90% R.H. and the corresponding (b) oxidized fibers and (c) PCF (carbonized) fibers.

Similarly, USAXS/SAXS pyrolyzed fibers profiles can be seen in Figure 5.8c. The fiber diameter feature is seen between 0.001 nm^{-1} and 0.03 nm^{-1} while the pore features are seen from 0.03 nm^{-1} to 5 nm^{-1} . At the lower humidity values of 40-50% R.H., pore features are seen at larger scattering vectors. At these humidity values, the scattering profile displays a broad peak shape,

indicating that the pores are weakly correlated. At the high R.H. values of 70-90%, larger pore features are observed at lower scattering vectors. At these humidity values, the scattering profile displays a knee shape with no upturn, indicating that the pores are relatively dilute. At the intermediate R.H. of 60%, no strong scattering is observed, perhaps indicating that no single morphology is dominant.

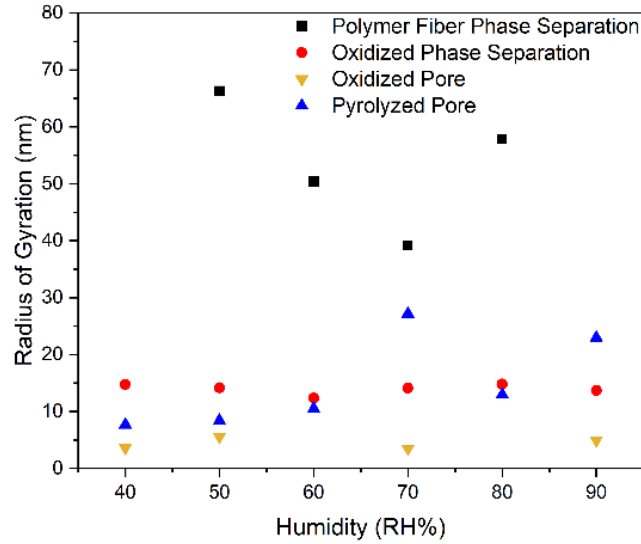


Figure 5.9. Radius of Gyration (unified fit) of the fibers in the as-spun polymer, oxidized, and carbonized states as a function of relative humidity from 40-90%.

Pyrolyzed samples were fit to the Unified Fit function. Pore radii of gyration of 7.6 nm and 8.4 nm were found for the 40% and 50% R.H. samples, respectively. Assuming spherical pores, the pore radii can be calculated using the following equation:⁷¹

$$R_g = \sqrt{\frac{3}{5}}R \quad (5)$$

The spherical radii for 40% and 50% then becomes 9.9 nm and 10.8 nm, respectively. These radii values agree with the porosimetry data, considering that Guinier approximation overestimates radius of gyration.⁷² The Unified Fit function was modified with the Born-Green closure to the Ornstein-Zernicke equation to capture the structure found in the 40% and 50% R.H. samples. The

correlation radius increases from 20.3 nm to 22.5 nm with increasing R.H. from 40% to 50%. Additionally, the packing factor decreases from 2.81 to 1.57 with increasing R.H. from 40% to 50%. These trends in radius of correlation and packing factor indicate that pore ordering begins to become disrupted as relative humidity increases to 50%. These trends agree with the disappearance of structure in the scattering pattern beyond 50% R.H..

Increasing relative humidity generally increases the radius of gyration of the pores (Figure 5.9), in agreement with the pore size distributions from nitrogen porosimetry. Similar to the BET and SEM results, the pore coalescence appears probably owing to the reorganization of PMMA which results in pore generation in the PCFs (Table S5.1). Interestingly, the largest pores, with a radius of gyration of 27.2 nm, are observed with the samples spun at 70% R.H.. This relative humidity may provide enough thermodynamic driving force to develop phases that are an optimal size and distribution for coalescence during pyrolyzation. At higher relative humidity, fewer pores are present along the sheath region of the fibers (Figure S5.6), yet the PMMA domains coalesce creating larger pore sizes (Figure 5.7), due to a less well-developed phase separation. Notably, the pyrolyzed pore radius of gyration ends up between the values for the oxidized phase separation radius of gyration and the oxidized pore radius of gyration for the low R.H. values (Figure 5.2). This observation may indicate that the pores are growing as the phases are shrinking and developing into pores. At the higher relative humidity values of 70% and 90%, the pyrolyzed pores are larger than the oxidized phase separation features. The coalescence of several pores may allow growth to larger sizes than the phase separation features. At 50% and 60% R.H., a smaller feature is seen between 1 and 5 nm⁻¹. This feature could indicate the presence of smaller pores (< 10 nm). Incidentally, the nitrogen porosimetry pore size distributions of the 50% and 60% R.H. pyrolyzed fibers also indicate an increase in the number of pores with widths smaller than 10 nm.

Mechanical properties of PCF. The varying porous structures within the PCF contributed to differing mechanical properties. As shown by tensile tests (Figures 5.10 and S5.8), the tensile strength was the lowest for 40% PCF and increased steadily with humidity up to 70% (Table S5.2). The tensile strength of 70% PCF was ~ 5-fold that of 40% PCF, and at least 2-fold of the rest PCF mats (Figure 5.10a). The 80% PCF exhibited the second highest tensile strength, but still only half the strength of the 70% PCF. As the humidity further increased to 90%, the tensile strength decreased. The toughness of PCF showed a trend similar to tensile strength, where the 70% PCF exhibited the highest (13 MPa) and 40% PCF the lowest (< 1 MPa) toughness (Figure 5.10b). Most PCF showed < 1% elongation, except the 70% PCF which exhibited 1.2% elongation (Figure 5.10c).

The development of a carbon sheath owing to polymer domain reorganization benefited the mechanical strength of certain PCF. Typically, low-humidity PCF (*i.e.*, 40% and 50%) lacked a continuous mechanically strong carbon structure present in conventional gel-spun PAN-derived carbon fibers.⁷³ Instead, they have a perforated carbon network around the pores. The network had “necking” regions, where stress could concentrate and reduce the overall axial resiliency during deformation.⁷⁴ The “necking” regions can be strengthened by tension during pyrolysis, similar to the tensioning conventional carbon fibers during the pyrolysis process.⁷⁵ As the humidity was increased from the ranges of 40-50% to 60-80%, a continuous long-range carbon sheath layer was developed in the PCF. The long-range carbon sheath layer increased the mechanical strength of the fiber mats. Particularly, the 60% and 70% PCF exhibited good flexibility despite the high porosity. The 80% PCF possessed low porosity and good flexibility, but the bead-and-clump formation, which was caused by the non-solvent precipitation, diminished the mechanical strength of the fiber mat. Our results agreed with observations in a previous report, where electrospun

PMMA fibers from DMF solutions showed a similar critical humidity level at 80% R.H.. At ~ 80%, the non-solvent effect reached a tipping point and it started to distort the fiber morphologies. Lastly, the 90% PCF lacked flexibility, likely because the carbon sheath layer was disrupted by the bead-and-clump structures induced by the severe non-solvent induced phase separation and polymer precipitation (Figure S5.7). In addition to the carbon sheath layer, USAX data indicated that the 70% PCF had the largest average fiber diameter, which also contributed to the strongest mechanical strength (Figure S5.10). Overall, the 70% PCF showed the highest flexibility because of the continuous carbon sheath and large fiber diameter (Video S1).

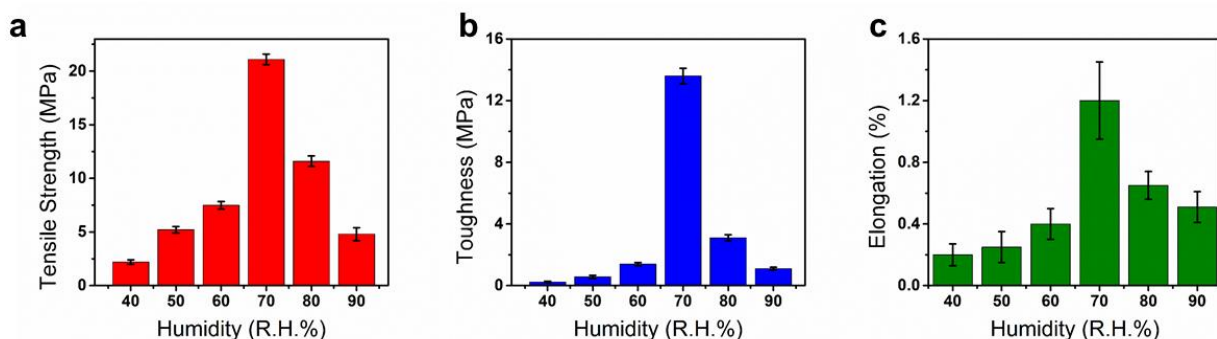


Figure 5.10. DMA histograms for the 40-90% PCF after stress/strain calculations for (a) tensile strength, (b) toughness, and (c) elongation.

Electrochemical performance of PCF. Owing to the conductivity of graphitic carbon, PCF has excellent potential in energy storage devices. The gravimetric capacitances of all PCF were examined in a 3 M KOH aqueous solution using a three-electrode cell with an Ag/AgCl reference electrode. At a 10 mV s^{-1} scan rate, the 40–70% PCF displayed the highest capacitances of $\sim 300 \text{ F g}^{-1}$ (Figure 5.11a). However, capacitance dropped by roughly half for the 80% PCF (153 F g^{-1}) and by another half for the 90% PCF (71 F g^{-1}). The scan rate capacitance of the PCFs followed tantamount trends across the range of $10\text{--}1000 \text{ mV s}^{-1}$ (Figure 5.11b). Surface area correlates positively with the electric double-layer capacitance of porous materials. Because of the similar

surface areas (difference within $\pm 16 \text{ m}^2 \text{ g}^{-1}$ from the average), the capacitance of PCF 40-70% were comparable (difference within $\pm 12 \text{ F g}^{-1}$ from the average) (Figure S5.11). Additionally, there was pseudo-capacitance contributed by the N and O heteroatomic doping, which resulted from PAN and the oxidation.

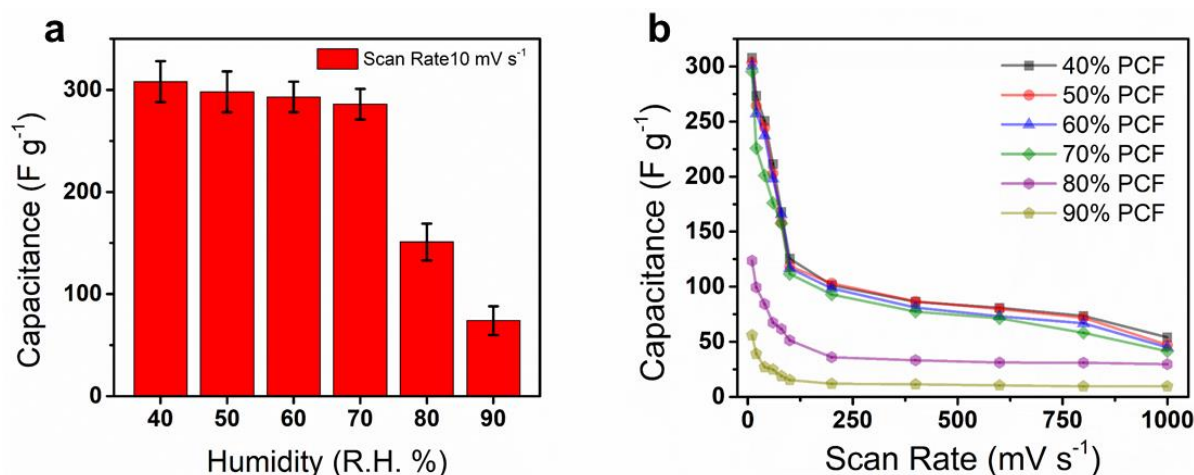


Figure 5.11. Electrochemical gravimetric capacitance of PCFs in 3 M KOH solution. (a) Histogram of gravimetric capacitance of PCF vs. relative humidity at a scan rate of 10 mV s^{-1} . (b) Scan rate capacitance for PCF in the range of 10 - 1000 mV s^{-1} . The legend represents the relative humidity during electrospinning of the fibers.

Based on the physical, mechanical, and electrochemical performance of the PCF, the electrodes were investigated for use in flexible supercapacitors. The 40% and 70% PCF were evaluated within a polyelectrolyte cell of PVA/KOH wrapped by parafilm. The electrodes were bent at various angles between 0 and 180° and the capacitances were measured with cyclic voltammetry (Figure 5.12). At 0° , both 40 and 70% PCF exhibited congruous specific capacitances of $239 \pm 12 \text{ F g}^{-1}$ and $249 \pm 13 \text{ F g}^{-1}$, respectively. At 90° , however, only the 70% PCF retained the same performance while the 40% PCF dropped its capacitance by $\sim 82\%$ (Figure 5.12a). At 180° , the 70% PCF retained the structure and capacitance of $249 \pm 20 \text{ F g}^{-1}$ whilst the 40% PCF reduced

further down to $22 \pm 14 \text{ F g}^{-1}$. Ultimately, the 70% PCF provided reliable gravimetric capacitances upon being bent at various angles, whereas the 40% PCF lost the energy storage capabilities. The 70% PCF were then subjected to bend angles of 0° , 45° , 90° , 135° , and 180° at scan rates of $10 - 1000 \text{ mV s}^{-1}$ (Figure 5.12b). The 70% PCF showed a $52 \pm 4\%$ retention capability regardless of the bending angle. One consideration for the flexible electrodes was the ability to survive repeated bending. The 70% PCF were bent between 0° to 180° for 50 cycles, and the capacitances were measured at 20 mV s^{-1} (Figure 5.12c). At the 50th bend, the fibers showed $\sim 99\%$ capacitance retention (Figure 5.12c). Two in-series capacitors made of $\sim 3 \text{ mg}$ of 70% PCF provided a voltage of $\sim 2.2 \text{ V}$ and were able to light a simple LED (Figure 5.12e). Although rudimentary, the PCFs demonstrated the capability for developing advanced flexible electronics, where PCFs can serve as both structural support and energy storage media.

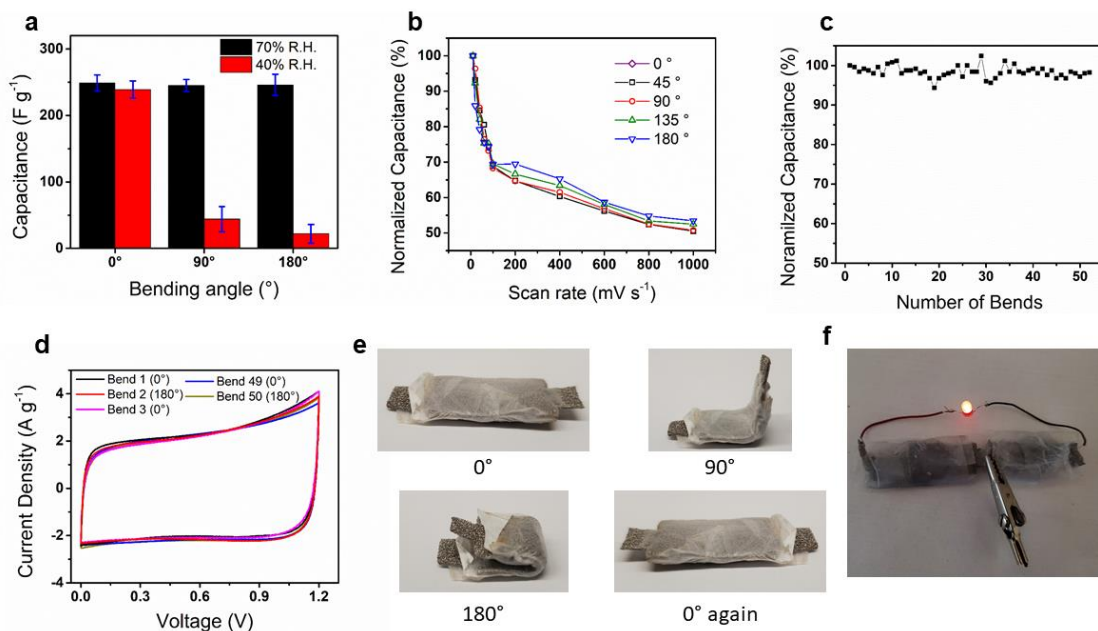


Figure 5.12. Electrochemical performance of the carbon fibers within gel-state electrolyte (PVA/KOH). (a) Gravimetric capacitance of 40% and 70% PCF at 0° , 90° , and 180° at a 10 mV s^{-1} scan rate. (b) Rate capacitance of the 70% PCF at bending angles of 0° , 45° , 90° , 135° , and 180° at scan rates of $10 - 1000 \text{ mV s}^{-1}$. (c) Normalized capacitance for the 70% PCF upon repeated 180° at scan rates of $10 - 1000 \text{ mV s}^{-1}$.

bending and (d) representative CV curves at 20 mV s^{-1} in the first three and last two bending cycles. The bending angles are shown in the parentheses. (e) Photographs of a capacitor made of the 70% PCF bent at angles of 0° to 90° , 180° and back to 0° . (f) A photograph of a lit LED bulb with two PCF capacitors in-series.

5.5 Conclusions

Block copolymer derived PCF hold significant promise in developing advanced structural energy materials. Electrospinning conditions of the polymer fibers provided a way to tune the mechanical and electrochemical properties of PCF. In conjunction with block copolymer microphase separation, the use of a non-solvent such as water vapor jointly controlled the porosity and mechanical properties *via* VIPS. In the low-humidity range (40-50% R.H.), water vapor showed little effect and PMMA-*b*-PAN fibers underwent microphase separation which developed into mesopores with narrow pore width distributions. In the mid-humidity range (60-70% R.H.), water vapor provided enough driving forces to initiate a VIPS effect, reorganizing the PAN and PMMA domains to form a core-sheath structure in the fibers. Lastly, in the high humidity range (80-90% R.H.), the fibers experienced strong vapor induced phase-separation and even precipitation, forming large polymer clusters and thus non-uniform pores in the PCF that severely weakened the mechanical strength. The electric double-layer capacitance favored the lower humidity owing to the higher surface areas. The juxtaposition of both flexibility and electric double-layer capacitance existed at 70% R.H., showing a window for PCF to achieve both electrochemical and mechanical properties. Fabricated into flexible capacitors, the 70% PCF demonstrated the capability of serving as structural energy storage materials. The morphological study herein provides a systematic understanding of non-solvent effects on electrospun block copolymer fibers and the resulting PCF.

The flexible block copolymer-derived PCF underscore the potential in flexible electronics, energy storage, and environmental science.

5.6 Supplemental Information

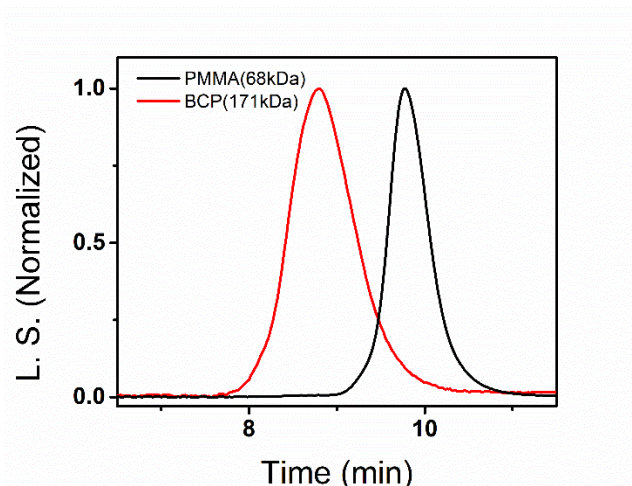


Figure S5.1. Size-exclusion chromatography profile with the macro PMMA-CTA, and the PMMA-*b*-PAN block copolymer (BCP) using a light scattering detector.

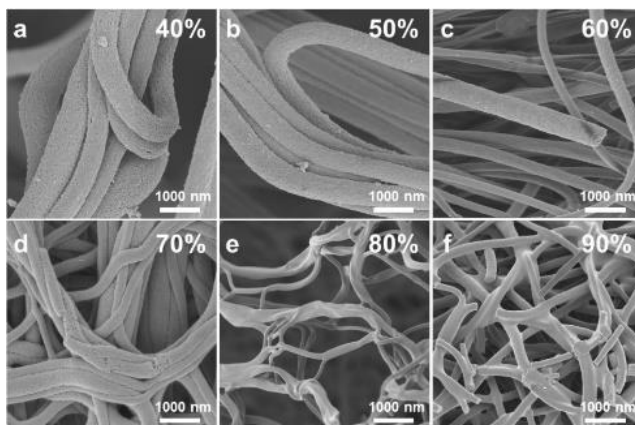


Figure S5.2. Representative SEM images of the polymer fibers (a-f) after electrospinning within the humidity treated box from 40% - 90% R.H..

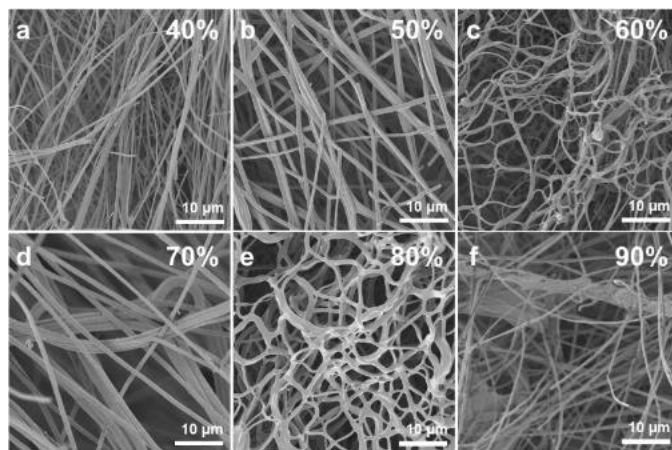


Figure S5.3. Representative SEM images of the polymer fibers (a-f) after electrospinning within the humidity treated box from 40% - 90% R.H..

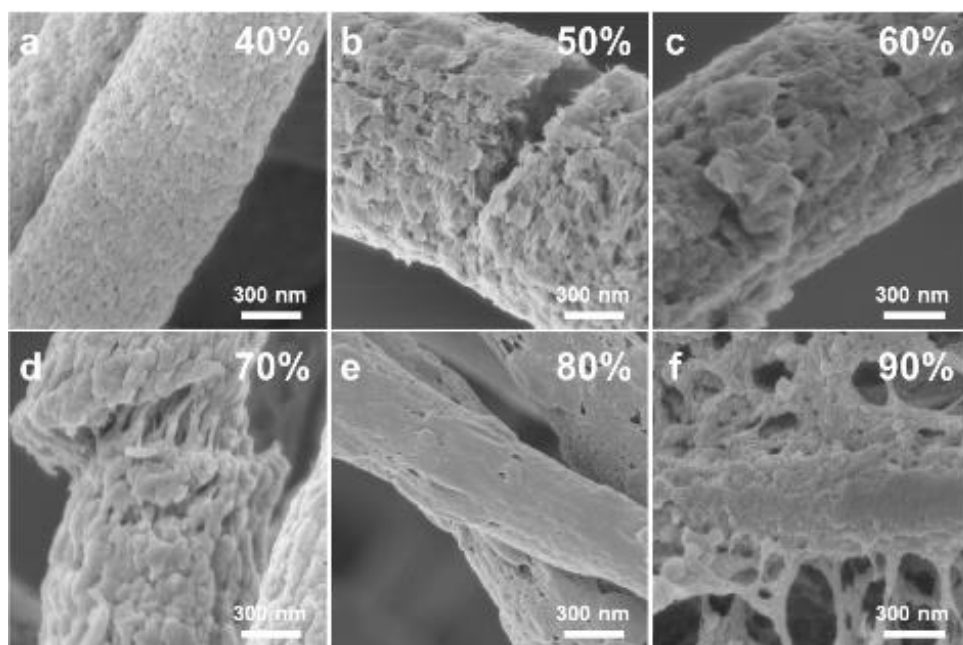


Figure S5.4. Representative SEM images of the oxidized fibers (a-f) after electrospinning within the humidity treated box from 40% - 90% R.H..

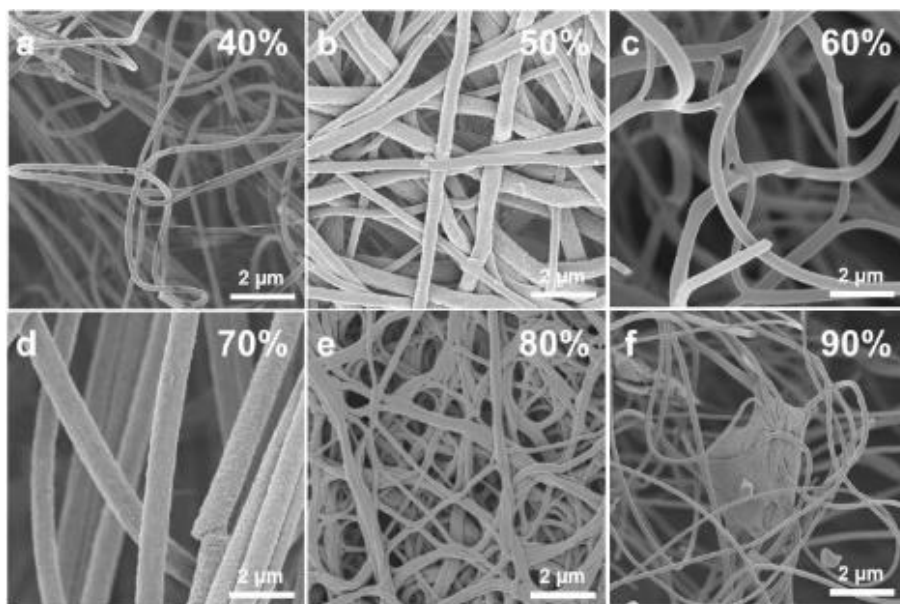


Figure S5.5. Representative SEM images of the oxidized fibers (a-f) after electrospinning within the humidity treated box from 40% - 90% R.H..

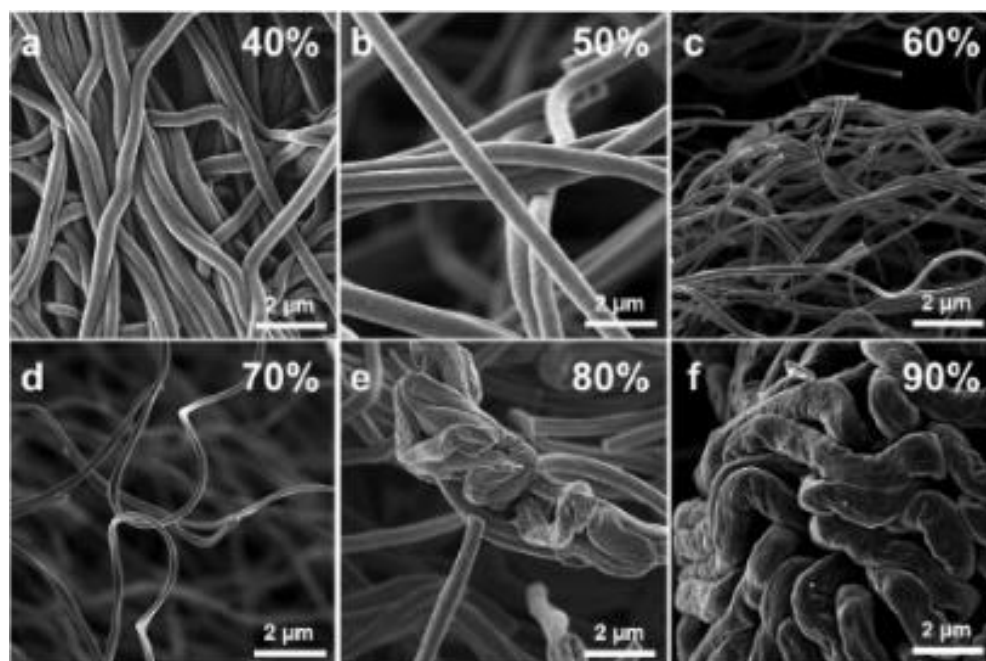


Figure S5.6. Representative SEM images of the carbonized fibers (a-f) after electrospinning within the humidity treated box from 40% - 90% R.H..

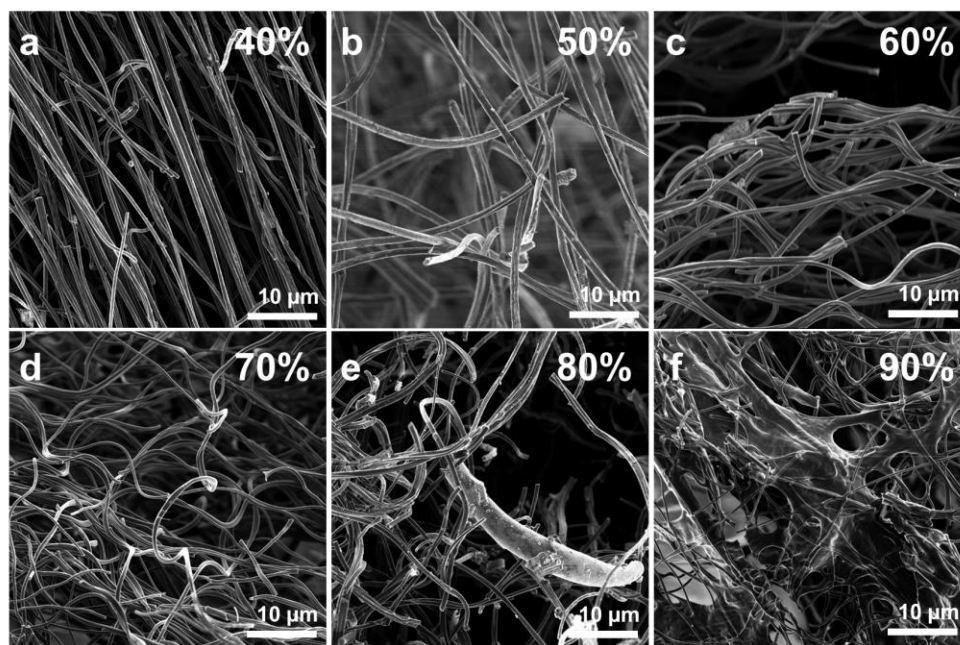


Figure S5.7. Representative SEM images of the carbonized fibers (a-f) after electrospinning within the humidity treated box from 40% - 90% R.H..

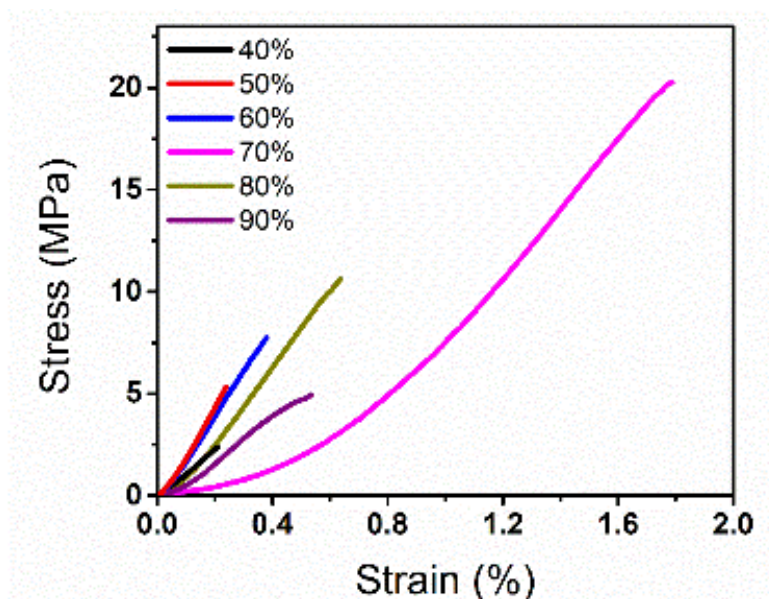


Figure S5.8. Representation stress/strain curve using dynamic mechanical analysis for humidity treated fibers 40-90% R.H..

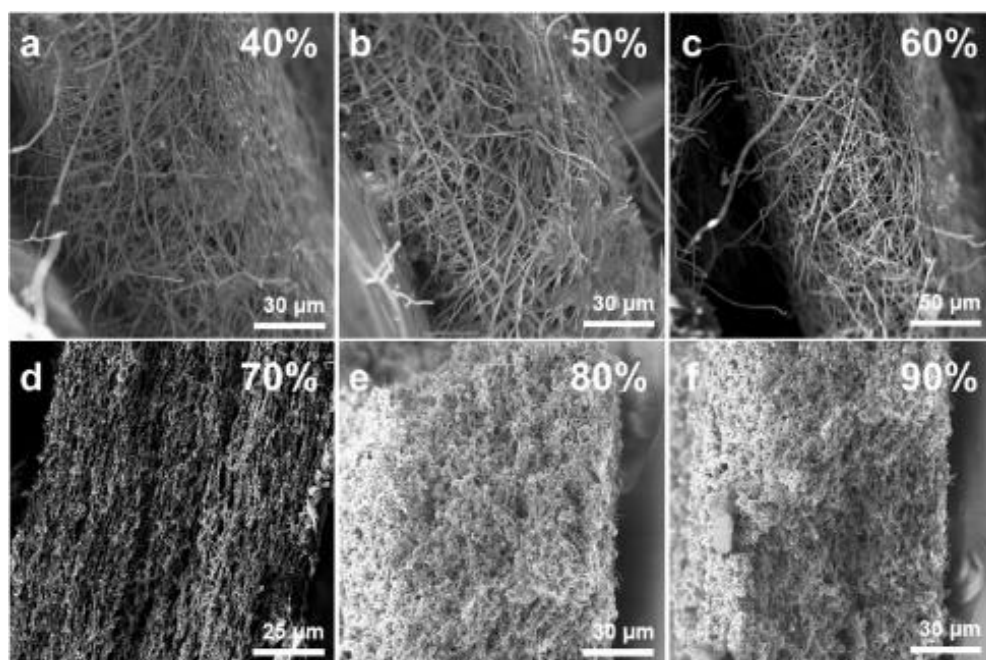


Figure S5.9. Fiber mat cross section SEMs used for dynamic mechanical testing for humidity treated fibers 40-90% R.H..

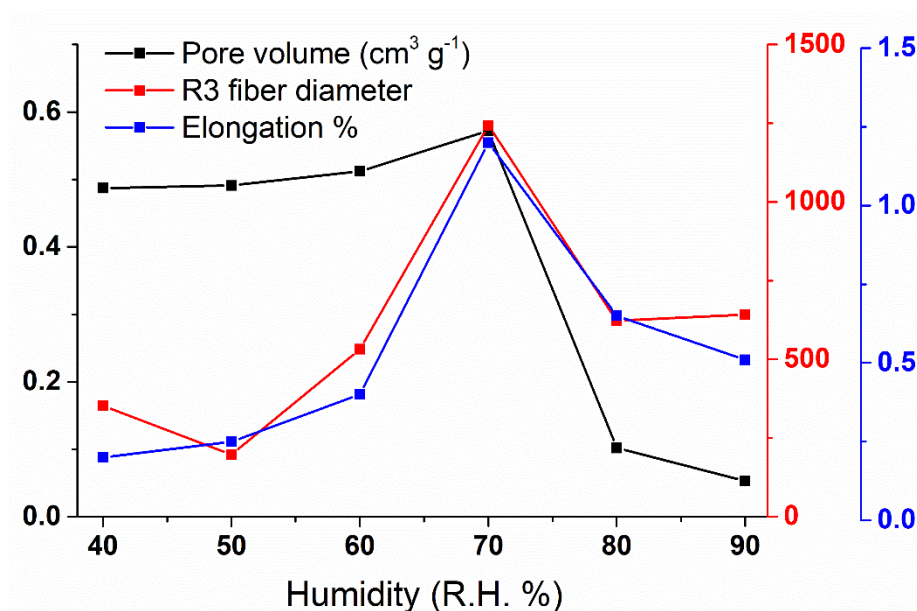


Figure S5.10. The humidity treated carbon fibers were plotted with respect to pore volume calculated from nitrogen physisorption, Level 3 of the unified fit from USAXS, and elongation % determined from DMA.

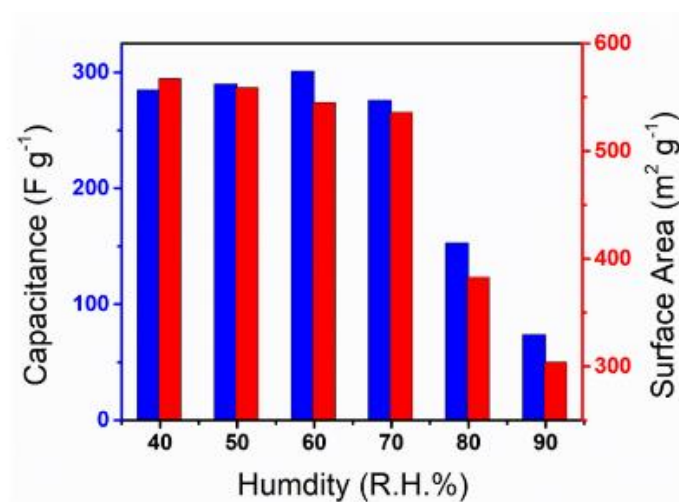


Figure S5.11. Physisorption data for surface area compared to gravimetric capacitance in aqueous solution.

Table S5.1. Unified Fit function output. Levels were selected and grouped for ease of comparison. Level 1 indicates the smallest feature in the series. Level 1 indicates the phase separated domain size for the spun polymers, the supposed pore size for oxidized fibers, and the smallest pore level observed in pyrolyzed fibers. Level 2 indicates the next largest level observed in a series. Level 2 indicates the phase separated domain size for oxidized fibers and the larger pore size for pyrolyzed fibers. Level 2 is omitted for the spun polymer series, such that level 3 may be reserved for the fiber diameter feature for each series.

Series	R.H.%	R _{g1} (nm)	P ₁	R _{g2} (nm)	P ₂	η_2	pack ₂	R _{g3} (nm)	P ₃
BCP fiber	40							536	3.719
BCP fiber	50	66.3	3.73					676	3.757
BCP fiber	60	50.4	3.73					556	3.776
BCP fiber	70	39.2	3.74					780	3.879
BCP fiber	80	57.9	3.72					710	3.857
BCP fiber	90							560	3.766
Oxidized Fiber	40	3.65	2.384	14.8	4			543	3.891
Oxidized Fiber	50	5.60	3.5	14.2	4			478	3.88
Oxidized Fiber	60			12.4	3.654			468	3.9
Oxidized Fiber	70	3.48	2.47	14.1	4			332	3.87
Oxidized Fiber	80			14.8	3.766			378	3.81
Oxidized Fiber	90	4.97	4	13.7	4			493	3.882
PCF	40			7.6	4	20.3	2.814	353	3.76
PCF	50	2.17	2.852	8.4	3.5	22.5	1.574	197	3.784
PCF	60	0.71	1.822	10.5	3.212			532	4
PCF	70			27.2	4			1243	3.803
PCF	80			13.0	3.726			623	3.741
PCF	90			23.0	4			642	3.707

Table S5.2. DMA data based on stress strain mechanical evaluation.

Humidity (R.H.%)	Tensile Strength (MPa)	Elongation (%)	Young's Modulus (MPa)	Toughness (MPa)
40	2.2 ± 0.2	0.20 ± 0.05	11.5 ± 0.4	0.25 ± 0.05
50	5.6 ± 0.2	0.30 ± 0.06	18.8 ± 0.5	0.59 ± 0.11
60	7.9 ± 0.3	0.40 ± 0.06	15.9 ± 0.4	1.4 ± 0.1
70	21.2 ± 0.5	1.10 ± 0.11	18.8 ± 1.0	13.6 ± 0.4
80	11.5 ± 0.4	0.60 ± 0.07	10.2 ± 0.4	3.1 ± 0.2
90	4.4 ± 0.2	0.50 ± 0.05	5.3 ± 0.3	1.1 ± 0.1

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Chapter 6. Conclusions and Perspective

6.1 Summary of the Work Completed

In this dissertation we have studied block copolymer synthesis, capacitive deionization, solar desalination, nano-confinement effects on water evaporation, and humidity effects on polymers electrospinning. Herein, a summary of the conclusions and perspective work is presented.

6.1.1 *Composition design of carbon derived block copolymers*

Compositional design of poly(methyl methacrylate)-*block*-poly(acrylonitrile) (PMMA-*b*-PAN) defines the microphase separation within the polymer fiber. The range of molecular weights and volume fractions were determined to control to a tunable scale of pore sizes, surface areas, and subsequent physical and electrochemical properties. Notably, at similar volume fractions, but longer chain lengths of PMMA, the pore sizes increase owing to the conglomeration of the PMMA domain. PAN domains which develop into carbon showed no contribution to mesopore development, and only provided micropores from missing graphitic carbon layers. The volume fraction around 50% showed the highest surface area and subsequent highest gravimetric capacitance. Overall, this work contributed to the understanding of block copolymer design in electrospun porous carbon fiber fabrication, namely by showing the controllable physical properties based on radical polymerization.

6.1.2 *Organic dye removal using porous carbon fiber*

The electrochemical prowess of the block copolymer derived carbon fibers provided a platform to investigate mesopore technology on capacitive deionization. Using the tunable mesoporous carbon fibers, pollutant removal was investigated through electrosorption. Specifically, two organic charged dyes underwent electrosorption within the carbon fibers. The contact time and mass of dye removal was studied using isotherm and kinetic models, including queso-first order, queso-second order, and Weber-Morris (intra-particle) kinetic models. The rate of adsorption exhibited second order kinetic characteristics and showed a high fidelity to the Weber-Morris model. Indicatively, the Weber-Morris model provided insights into the rapid diffusion capabilities

of the carbon fibers which validates the inter-connected porous structure originally suggested in literature. Additionally, the second stage fitting of the model suggested the highly accessible surface area (termed effective surface area) which provides an understanding of ionic flux within the mesopore-micropore matrix. Langmuir modeling determined a theoretical maximum adsorption of 1680 mg g^{-1} of dye and highly robust electrical cycling of the carbon fibers. The material provided an understanding of the surface area energies with regards to adsorption modeling. Thus, this work lays a foundation for future environmental applications which utilizes interconnected porous systems.

6.1.3 Reduction in Water Vaporization Enthalpy by Block Copolymer-Based PCF

Emerging nanotechnology seeks to leverage novel material design for overcoming challenging resource acquisition which are rapidly rising into a global crisis. Access to clean water looms on the precipice of a society as a larger population and depletion of resources being to outweigh current technological capabilities. The water evaporation studies based on mesoporous carbon fibers provides insight into how to overcome some of the clean water limitations. Our investigation observed the enthalpic contributions to water evaporation within the confines of a carbon fiber mat with pore sizes from $\sim 1 - 22 \text{ nm}$. The fiber mats not only achieved a high desalination rate ($3.8 \text{ kg m}^{-2} \text{ h}^{-1}$), but more importantly, the fiber mats allowed a study into enthalpic efficiencies within the hydrogen bonding network confined in the mesopores. We added to the discourse of nano-confinement effects by comparing micropore fibers ($< 2 \text{ nm}$) with hierarchical porous fibers (meso and micro pores). Ultimately, the enthalpic energies for evaporation was reduced by $\sim 48\%$ of bulk water properties, with the use of $\sim 11 \text{ nm}$ mesopores in conjunction with micropores and inter-fiber distances. We attributed the enthalpic energies reduction to the breaking of hydrogen bonds and overall reduction in water density, which lead to less energy requirements for water-steam phase transitions. The contributions from pore sizes not only allows this achievement into solar desalination, but also promote future nanotechnology for clean water, energy, and environmental applications.

6.1.4 Humidity effects on electrospun block copolymers for flexible electrodes

The block copolymer carbon fibers show resounding properties for energy storage; however, the structural stability and mechanical properties had not been elucidated. The non-solvent vapor treatment for block copolymer electrospinning as well as its effect on fiber structural and fiber mats mechanical performances was systematically studied. Since the individual blocks of PMMA and PAN possessed differing surface energies, the polymer domains reorganized based on the presence of nonsolvent. In low (40-50%) humidity the solvent rapid evaporates from the fiber, which leads towards a kinetically trapped morphology and excellent microphase separation. In medium (60-70%) humidity, the polymer chains to reorganize into large domains and preferential PAN exterior and PMMA interior reorganization. Finally, the high (80-90%) humidity developed non-solvent precipitation effects which rapidly develop into beads and large clusters of polymers which compromised any beneficial physical or structural properties. In particular, we optimized the humidity treatment system and identified the region to achieve flexible carbon fibers, while still maintain a sufficiently ordered microphase separation of the polymer precursor to preserve the unimodal mesopore development and subsequent high surface area.

6.2 Perspective

6.2.1 Polymerization synthesis for oxygen tolerant block copolymers

Motivation. We have provided a platform for tailored carbon fiber nanotechnology, as well as a fundamental study into hierarchical porous structures. The initial synthesis using reversible fragmentation chain transfer (RAFT) polymerization allows the controllable block chain lengths. The systematic RAFT study exhibited the ranges and structures of controlled polymeric fibers. However, certain research into streamlining the polymerization process would behoove future applications requiring larger carbon fiber yields.

Currently the RAFT approach requires an oxygen free environment which in turn limits batch size, speed, cost, and safety. In response, several alternative polymerization pathways could be explored with this block copolymer and also alternative sacrificial blocks in the self-assembly system might be substituted. Emerging studies include oxygen-tolerant radical polymerization by using photoinitiation, oxygen initiation, and various anthracene mediators.

Hypothesis. By applying systematic studies under new initiators, mediators, and monomers, a direct and facile method for polymerization might be discovered. Currently, an oxygen tolerant fabrication method for this specific block copolymer is not investigated. The next step in this work includes achieving “living additive manufacturing” open to air, or at least developing an oxygen tolerant polymerization. The difficulty will lie in ensuring the block copolymer formation, and the control of molecular weight and retaining a low poly dispersity. In addition, some pathways will alter end groups which are unknown in their impact for electrospinning fibers and carbonization. By investigating into these synthetic methods, a new branch of work can continue into applying porous carbon fibers in many practical energy and environmental applications.

Research plan. The process I propose for future studies to develop a facile and scalable block copolymer synthesis focuses on two pathways. These pathways focus on ensuring the polymerization process for both methacrylate and acrylonitrile, which become a narrow target with current methods. The first pathway I propose is on Activators ReGenerated by Electron Transfer (ARGET) atom transfer radical polymerization (ATRP) (**Figure 6.1a**). Specifically, I suggest looking at three different combinations which might achieve the designed block copolymer development. The complex of Cu(II)Br₂ with N, N, N', N'', N''-pentamethyldiethylenetriamine (PMDETA) as a reducing agent and placed in ionic liquids has previously shown oxygen tolerance with the ability to polymerize without other additive.¹ Although the flask may still need to be sealed and the procedure is not proven for PMMA-*b*-PAN yet, the ability to polymerize both methacrylate and acrylonitrile are theoretically possible.^{1,2} In light of that, two other approaches might successfully copolymerize the desired block copolymer. Previous studies show polymerization of PMMA with ARGET-ATRP including Fe(III). The first with Sn(EH)₂ as a reducing agent which can develop up to two blocks in solution.³ The second including Fe(III)Br₃ with ascorbic acid as a reducing agent, and this combination has worked in DMF which parallels our previous work.⁴ Both approaches might overcome the challenges of oxygen requirements, however systematic studies are still required for ligand compatibility. The ARGET-ATRP approach will develop complications that are different than the RAFT process that we have studied, however the ability to create block copolymers without arduous oxygen removal should not be discounted. The ligand design and the solutions will play a critical role in the synthesis, although referencing previous work will help expedite the process.⁵ The combination therein would advance not only the polymer synthesis field but also the development of scale-up porous carbon fibers.

The last alternative method I will purpose is photoinduced electron transfer (PET) reversible fragmentation chain transfer (RAFT) (**Figure 6.1b**). Previous studies show the viability for re-initiation and subsequent monomer addition.⁶ Which photocatalyst and which solvent system that will provide a sufficiently quick regeneration mechanism may require systematic studies especially for the second block polymerization.⁷ The application in acrylates are readily available, however developing a system to directly add acrylonitrile as a secondary block might prove difficult, due to compatibility between both blocks. Iridium (III) chloride compounds allow for reintroducing radicals which begin the polymerization process prior to recombination occurring. Notably, the solutions must be in non-aqueous solvents as to avoid insolubility detrimental effects. The use of emulsifiers and stabilizers might facilitate the block addition of PAN with PMMA.⁸

Although this direct synthetic pathway remains unproven, there are excellent initial studies from which the polymerization progress of this carbon fiber precursor may benefit. The processing by oxidation and carbonization would proceed as normal. Overall, the functionality of oxygen tolerant methods will improve the ability to apply carbon fibers into larger scale research, gaps in future projects.

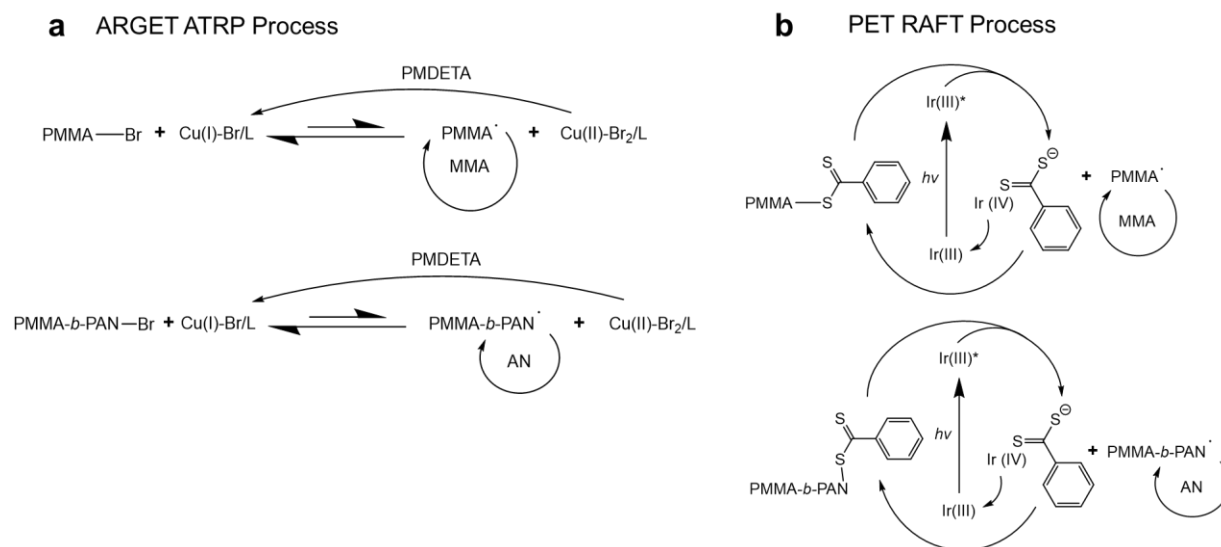


Figure 6.1 Synthetic pathways for (a) ARGET ATRP polymerization including poly(methyl methacrylate) (PMMA) and poly(acrylonitrile) (PAN) with Cu-ligand bind and reduction with N, N, N', N'', N''-pentamethyldiethylenetriamine (PMDETA) and (b) PET RAFT polymerization for PMMA and PMMA-*b*-PAN using a photo-induced Ir compound for radical generation.

6.2.2 *Synthetic routes towards catalytically active porous carbon*

Motivation. Another avenue of research which would greatly contribute to the carbon fiber field, is development into catalysis capabilities. Porous carbon fiber possesses the unique characteristics to develop highly dispersed catalytic sites and catalytic activity that desirable for specific catalytic pathways, owing to its unique surface chemistry.^{9, 10} First, direct embedded point catalysis within the carbon fiber graphitic structure might prove successful. Certain mechanisms for developing catalysis require defect points for insertion of active metal sites. Here carbon fibers possess three key elements which can be targeted, oxygen, nitrogen, and void sites. Previous work looks at using graphene sheets with high energy input for impregnation of iron sites.¹¹

Hypothesis. Since the carbonization process of PAN already develops missing carbon sites (micropores), the attachment sites become available throughout the porous material. Moreover, the addition of oxygen groups within the carbon fiber will help to stabilize the implantation of catalysis material.^{12, 13} Stabilization will be the biggest factor to overcome in designing these confined space catalysts. Specifically, the coordinatively unsaturated metal sites require synergistic stabilizing to retain catalyst activity. The oxygen and nitrogen groups within the carbon fiber will provide a three-fold benefit, (1) impregnation assistance for coordinating catalyst material to the surface, and (2) conjugation of the catalytic site for retaining unsaturation (3) dispersion of catalysis sites.¹⁴

Research plan. Although there are several metal candidates for catalysis work, I propose two initial catalysis material to impregnate the graphitic carbon. First, application of iron phthalocyanine into iron-nitrogen sites along the carbon fiber might prove highly effective (**Figure 6.2a**). Iron phthalocyanine (FePc) stabilizes in the presence of oxygen sufficiently to bind into graphitic carbon structures.¹⁵ Owing to this, the oxygen sites on carbon fiber will aid in FePc implementation. Oxygen plasma and peroxide treatments which increase the oxygen saturation of the carbon surface will increase the mass loading, though dispersion studies might also be required. The Fe structure will also require maintaining coordinatively unsaturated sites within the carbon fiber structure.¹⁵ Fortunately, the oxygen and nitrogen assist in maintaining unsaturated sites for the Fe compound. These facets will provide pathways for several attenuations into oxygen reduction reactions, especially with the potential for studies into electrocatalysts thanks to the highly conductivity of carbon fiber.¹⁶

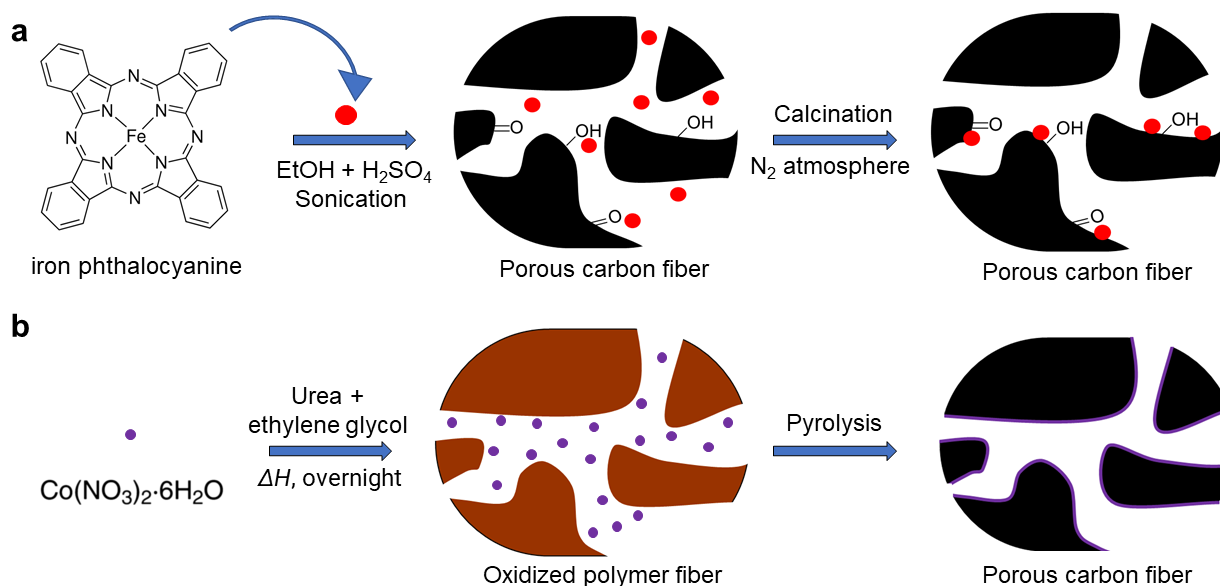


Figure 6.2 Metal catalysis doping into porous carbon fiber. (a) Iron phthalocyanine being dispersed into carbon fibers in ethanol by sonication with subsequent pyrolysis in inert atmosphere. (b) Cobalt deposition by heating a solution of ethylene glycol and urea overnight and subsequent annealing in air for 8 hours.

Cobalt-carbon systems appear to show promising results in electrocatalysis activities.¹⁷ Here, the integration of Co compounds is similarly enhanced by the unique structure of the carbon fibers. Additionally, assistances of oxygen-rich and nitrogen-rich precursor will be required to aid in Co site development along the carbon structure.¹⁸ Importantly for the function of Co electrocatalyst, porous polyhedron serves as an effective matrix for functionality.^{19,20} Similarly, the available edge sites in porous carbon fibers are enhanced for embedding layering Co (**Figure 6.2b**). These edge sites with the porous regions allow for highly diffusive activity within an aqueous or alkaline solution medium.²¹ In addition, the confinement effects of Co sites have shown the ability to develop more highly active quasi single sites.²² The nanopore catalytic activity would be enhanced by the hierarchical porous structure in PCF. The integration of Co also would directly align with the current fabrication methods of carbon fibers.²³ Synthesis of catalytically active PCF might be achieved with cobalt sites by introducing a precursor of Co(NO₃)₂·6(H₂O) prior to pyrolysis.²⁴

Notably, the pyrolysis temperatures will need to be studied for the highest yield of catalytic yield, most probability between 400 – 800 °C. A primary starting reagent mixture could be ethylene glycol with urea. With chemical and thermal processing, the surface of the carbon fibers should develop cobalt oxide layers. The studies of Co-PCF development should include hydrogen evolution reactions.²⁵ Given the electrical conductivity of the carbon fibers as well as the integration of catalytic sites, superior hydrogen evolution in alkaline solutions might be possible. Given both this and the aforementioned pathway, the carbon fibers might prove invaluable for insights into single atomic sites on porous carbon fibers.

6.2.3 Solid-electrode composite fabrication

Motivation. We highlighted the ability to create more flexible and robust carbon fiber which retains electrochemical capabilities, targeting on structural electronics and wearable electronics. The polymer chain reorganization will drastically affect the functionality of the resulting fibers. The development of flexible energy storage devices would gain great insight with the application of conductive polymer structures which can serve as an electrolyte material for high-end devices. Certain polymers such as polyaniline (PANI) can serve as excellent scale up material for porous carbon fiber-based supercapacitors.²⁶ However, PANI typically has a reduced life cycle owing to structural degradation during repeated charge/discharge.²⁷ Some attempts to mitigate decomposition include nano-fillers and other stabilizers as composites, including reduced graphene oxide.²⁸ By understanding the mechanism of stabilization, the porous carbon fibers might fill in the gap for longer life cycle polyelectrolyte-based supercapacitors.

Hypothesis. PANI has been studied as a compatible material for other carbon-based electrodes. By applying the vapor induced phase separation discussed, the porous carbon fibers will have a flexible structure which the PANI can interact with. The most direct approach to integration would be electrospinning the PANI with the block copolymer.²⁹ However, the morphological effects with humidity remain limited in understanding.

Research plan. The benefit of electrospinning simultaneously lies in the ability to compress the material for increased contact and reduced resistivity (**Figure 6.3a**). PANI will require stabilization prior to carbonization to retain functionality. Nickel oxide assists in thermal stabilization in air, and with inert atmosphere will further improve PANI retention.³⁰ Several studies can branch from this work for creating a continuous electrode layer combined with the

polyelectrolyte. Their intertwined nature allows for caging of the PANI and reduction in swelling during charge/discharge.³¹ If, however, this proves to be too challenging, an indirect approach would be to polymerize PANI onto the carbon fibers using *in-situ* polymerization.³¹ The porous carbon could then directly house the PANI within the fiber matrix. The polymerization will require precise control, as too much polymerization of PANI may fill the pores and reduce effective surface area. Electrochemical polymerization might provide the most effective method for electrolyte insertion into the porous carbon fibers (**Figure 6.3b**).³² Notably, the carboxyl groups assist the polymerization and allow a direct contact for PANI chains to the carbon surface. The carbon fibers might require oxygen plasma or peroxide treatment for an increase in the number of carboxyl groups available.³³ The benefit of the *in-situ* polymerization lies in the redox stability of PANI with a rigid carbon structure surrounding the conductive polymer. Overall, there are several projects which may successfully arise from integration of PANI or other polyelectrolytes into the flexible carbon fibers.

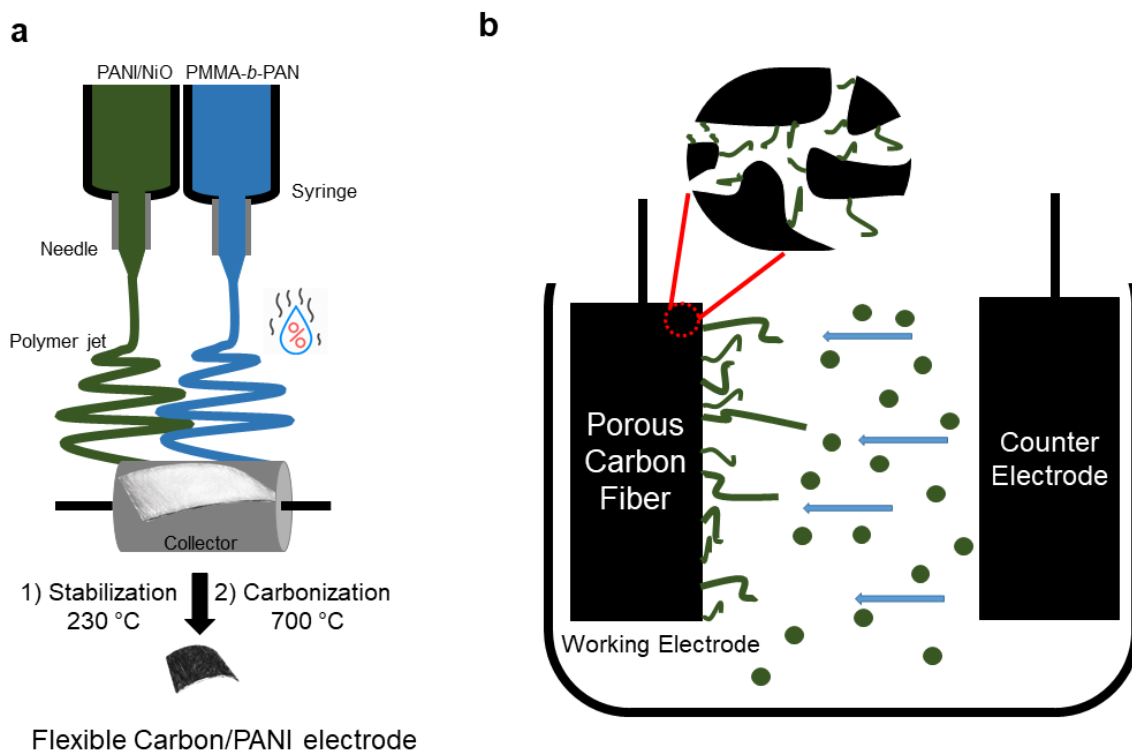


Figure 6.3 (a) PANI/NiO solution in a dual-spinner system with a block copolymer (BCP) electrospun in humidity onto a collection drum. The composite fiber mat is processed through stabilization and carbonization for a flexible carbon electrode. (b) Electrochemical *in-situ* polymerization of aniline into PANI within porous carbon fiber.

6.2.4 *Conclusions*

Overall, the field of carbon material for energy and environmental sciences were discussed through previously literature, current presented research, and perspective future avenues. Currently, the large batch development of block copolymers limits a more expensive application to industrial methods. The controlled radical polymerization methods allow for high fidelity and low dispersity, however more facile and oxygen friendly methods are required. I have proposed a few pathways to allow oxygen tolerant polymerization for block copolymers. The discovery of fast through-put block copolymer synthesis will greatly expand both the polymer field as well as several material fabrications which have shown research scale promise in performance. Parallel, the energy production, and catalysis field seek to incorporate dispersed site points of non-precious metal points within electrically conductive matrices. Research into metal and transition-metal sites along the carbon fiber porous structure will aim at achieving economical and sustainable energy acquisition and needed compound conversion. Surface chemistry and control of chemical groups along the carbon matrix will prove imperative for maintain long life cycle of catalytic material. The nitrogen and oxygen sites both provide distinct structural support for various metal complexes which were discussed. With the incorporation of the complexes, hydrogen evolution, oxidation reduction, oxygen evolution, and electrocatalysis can be targeted by tuning the catalytic precursor.

Finally, energy storage grows in demand for structural integrity with implementation for medical devices, automotives, and rapid charge/discharge energy storage. I proposed two pathways in order to provide a fully carbon electrode with flexible and strong characteristics to withstand demands of structural electronics. By integrating pseudocapacitive material with an all-solid-state electrolyte, the carbon fibers provide a means for direct structural electrode fabrication. Overall, the use of porous carbon fibers contributes to the fields of energy and environmental sciences not only as a promising candidate as a functional material, but also as a means to investigate the fundamental properties of nano-scale porous confines.

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