Surface Functionalized Electrospun Cellulose Nanofilters for High-Efficiency Particulate Matter Removal

Shaohsiang Hung

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Surface Functionalized Electrospun Cellulose Nanofilters for High-Efficiency Particulate Matter Removal

A Thesis Presented

by

Shaohsiang (Joe) Hung

Submitted to the Graduate School of the University of Massachusetts Amherst in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE IN CHEMICAL ENGINEERING

September 2021

Department of Chemical Engineering
Surface Functionalized Electrospun Cellulose Nanofilters for High-Efficiency Particulate Matter Removal

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ABSTRACT

SURFACE FUNCTIONALIZED ELECTROSPUN CELLULOSE NANOFILTERS FOR HIGH-EFFICIENCY PARTICULATE MATTER REMOVAL

SEPTEMBER 2021

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The global spread of COVID-19, as well as the worsening air pollution throughout the world have brought tremendous attention into the development of materials that can efficiently capture particulate matter (PM). Traditional filters made from fabric, glass fibers, or melt blown fibers exhibit a low efficiency at removing sub-micrometer and nanoscale particles. Additionally, they exhibit limited performance in high humidity, high temperature environments. We suggest that the high porosity of filters composed of nanofibers could provide minimal obstruction to air flow, while their high tortuosity and surface area-to-volume ratio presents an excellent platform for particle capture. Electrospinning is a simple and well-studied process to produce randomly accumulated nano- and micro-scale diameter fibers. The main advantages of electrospun nanofibers include their tunable fiber morphology and diameter under specific electrospinning parameters, as well as the ease of post-process modification. Studies have demonstrated its promising applications ranging from tissue engineering, water purification to wearable electronics. Giving the tunable aspect of the process, various polymers were electrospun with different morphology and fiber diameter which all demonstrated high particle removal
efficiency. Cellulose was chosen as the base material for our study since it is the most abundant biopolymer and its affinity for further chemical modification.

In this study, the removal of nanoscale particles via in-house fabricated cellulose nanofilters is significantly enhanced by chemically functionalizing the fibers’ surface via the deposition of the bio-inspired glue polydopamine (PDA) and the polycation poly(diallyldimethylammonium chloride) (PDADMAC). Nanofilters were electrospun from cellulose acetate solutions before being regenerated to cellulose via an alkaline treatment. Cellulose nanofilters were then functionalized using only PDA or the codeposition of PDA with PDADMAC. Scanning electron microscope (SEM), Fourier transform infrared spectrometer (FTIR), and high-resolution X-ray photoelectron spectroscopy (XPS) were used to characterize the nanofilters. The effects of filter packing density, filter layering, and surface functionalization on their performance, i.e., their filtration efficiency, most penetrating particle size (MPPS), performance in a high humidity environment, and filter pressure drop were investigated. Furthermore, by introducing hydrophilic and hydrophobic nanofibers within a composite filter structure, the performance of the composite filter remained unchanged even in high humidity.
# TABLE OF CONTENTS

ACKNOWLEDGMENTS ........................................................................................................ iv

ABSTRACT ........................................................................................................................................ vi

LIST OF TABLES .................................................................................................................. x

LIST OF FIGURES ................................................................................................................. xi

LIST OF ABBREVIATION ........................................................................................................... xiii

CHAPTER

1. Introduction ................................................................................................................ 1
   1.1 Motivation and Defining Air Pollution ................................................................. 1
   1.2 Filter Capture Mechanism and Performance ....................................................... 2
   1.3 Electrospinning Process ...................................................................................... 4
   1.4 Electrospun Nanofilters for PM removal .............................................................. 6
   1.5 Objectives of this MS thesis ............................................................................. 8

2. Materials and Methods ................................................................................................. 9
   2.1 Materials and Chemicals ..................................................................................... 9
   2.2 Fabrication of Cellulose Nanofiber Mat ............................................................... 10
   2.3 Nanofiber Mat Functionalization ....................................................................... 10
   2.4 Materials Characterization ................................................................................ 11
   2.5 Particulate Matter (PM) Generation and Filtration Test ..................................... 11

3. Results and Discussions .............................................................................................. 12
   3.1 Characteristics of Cellulose and Functionalized Nanofiber Filters ................. 12
LIST OF TABLES

Table 1. Summary of the elemental data analysis of the high resolution XPS that provides surface chemical composition analysis of cellulose, PDA and PDADMAC electropun nanofilters .................................................................14
LIST OF FIGURES

Figure 1. Mechanisms of particle capture by fibrous media. Thick blue lines indicate air flow streamline. Grey circles represent fibers of the filter media........................................3

Figure 2. The schematic of the typical electrospinning apparatus, which composed of a syringe loaded with polymer solution, a high voltage supply and a metallic collector......5

Figure 3. FT-IR spectra for as-spun cellulose acetate, regenerated cellulose, and cellulose functionalized with PDA and PDADMAC nanofilters.....................................................13

Figure 4. XPS spectra of (a) survey scans including cellulose, PDA and PDADMAC nanofilters and high-resolution scan of N1s for (b) PDA (c) PDADMAC nanofilters as a function of binding energy (eV). .................................................................14

Figure 5. SEM images and fiber diameter distribution for (a) bare cellulose (b) 2 mg/ml PDA and (c) 2 mg/PDA + 2 mg/ml PDADMAC codeposited electrospun nanofiber mats (d) Mixed cellulose ester (MCE) control filter. Fiber diameter distribution display average fiber diameters and standard deviation ..............................................................................16

Figure 6. (a) Schematic diagram of single and multilayer electrospun nanofilters with different thickness. (b) Packing density as a function of total thickness for all cellulose nanofilters investigated in this work. (c) Fractional penetration as a function of particle electrical mobility diameter ranging from 20 to 400 nm for each single layer and multilayer nanofilters. Overall filtration efficiency is displayed in the upright corner.............17

Figure 7. (a) Filtration efficiency (b) Pressure drop and (c) Quality factor as a function of packing density for control, and cellulose nanofilter samples. Samples having total filter thickness around 330 and 150 µm are listed........................................................................................................18

Figure 8. (a) Filtration efficiency (b) Pressure drop and (c) Quality factor as a function of packing density for control, PDA and PDADMAC samples. All samples having total filter thickness around 330 µm. .................................................................................................................19

Figure 9. (a) Normalized particle size distribution for incense particles (upstream) and downstream particles for control, cellulose, PDA and PDADMAC nanofilters. (b) Summary of filtration efficiency (E%), pressure drop, quality factor and fractional penetration percent (P%) for 41.9 nm particle for Control, Cellulose, PDA, PDADMAC samples. Fractional penetration as a function of particle electrical mobility diameter ranging (c) from 20 to 200 nm and (d) from 20 to 100 nm for control, cellulose, PDA and PDADMAC nanofilters. Overall filtration efficiency is displayed in the upright corner..21

Figure 10. (a) Particle fractional penetration percent and filtration efficiency of cellulose nanofilters for each cycle of filtration. SEM images of cellulose nanofilters after (b) 20 and (c) 80 mins of filtration........................................................................................................23
Figure 11. (a) Fractional penetration as a function of particle size ranging from 20 to 900 nm. (b) Schematic diagram of Cellulose, Cellulose Acetate and Composite filter structure. (c) Contact angle measurements results for cellulose and cellulose acetate nanofilters. (d) SEM images of cellulose nanofilters after high-humidity test.
LIST OF ABBREVIATION

$C_{\text{down}}$: number of particles counts at filter downstream

CPC: condensation particle counter

$C_{\text{up}}$: number of particles counts at filter upstream

E%: filtration efficiency

FT-IR: Fourier transform infrared spectrometer

MCE: mixed cellulose ester

MPPS: most penetrating particle size

MVTR: moisture-vapor transmission rate

P%: fractional penetration

PDA: polydopamine

PDADMAC: poly(diallyldimethylammonium chloride)

$P_{\text{down}}$: pressure measured at filter downstream

PM: particulate matter

$P_{\text{up}}$: pressure measured at filter upstream

QF: quality factor

SEM: Scanning electron microscope

SMPS: scanning mobility particle sizer

XPS: high-resolution X-ray photoelectron spectroscopy

Z: filter thickness ($\mu$m)

$\alpha$: packing density

$\rho_f$: density of the filter material

$\Delta P$: pressure drop
1. Introduction

1.1 Motivation and Defining Air Pollution

In 2016, according to the World Health Organization (WHO), 91% of world’s population breathes polluted air meaning that it has a quality level that exceed the WHO limits. Each year, over 3.2 and 4.8 million deaths attributed to ambient and household air pollution, respectively.\textsuperscript{1-2} The current global spread of COVID-19 results from possible respiratory virus transmission that as of January 2021 has already caused almost \~100 million reported cases and 2 million deaths.\textsuperscript{5,6} The urgent need and evaluation for respiratory masks as well as in-door air filtration has brought tremendous attention into the development of efficient particulate matter (PM) capture. PM is composed of a mix of extremely small particles and liquid droplets and is often categorized by PM2.5 and PM10 based on its particle size. PM with an aerodynamic diameter smaller than 2.5 µm (PM2.5) poses the greatest threat to human health since they can easily penetrate into human lungs and bloodstream.\textsuperscript{3} Studies has shown long-term exposure to PM2.5 have adverse influences on cardiovascular system and may also increase morbidity and mortality.\textsuperscript{7-10} Common PM2.5 particles include inorganic matter (such as SiO\textsubscript{2}, SO\textsubscript{4}\textsuperscript{2-}, NO\textsubscript{3}-), organic matter (elemental carbon, carbon black), bacteria and viruses coming from diverse sources such as diesel engine combustion, soil dust, coal and agricultural fields buring.\textsuperscript{4} Currently, air filtration is still the most promising technique to protect us from air pollutant contamination. Traditional filters made from fabric, glass fibers or melt blown fibers exhibit low efficiency for sub-micrometer and nanoscale particles. In order to improve the filtration efficiency for traditional filter media, thicker media with higher pressure drop and
energy costs were usually chosen.\textsuperscript{3,12} Additionally, they exhibit limited application in high humidity, high temperature environments.\textsuperscript{3,14} Furthermore, the antibacterial properties of those filters are seldom discussed.

The surge in demand for personal protection equipment during the pandemic has triggered another broad discussion on how the current filters actually perform. Common outdoor protection materials such as N95 masks, surgical masks as well as homemade cloth masks were chosen by the public.\textsuperscript{6} However, the thermal-physiological comfort and filtration efficiency deteriorates overtime when large amount of water vapor is exhaled by the mouth and nose resulting in pore obstructions in the protection materials.\textsuperscript{11} Also, there is limited data available for the protection materials’ filtration efficiency as a function of different aerosol sizes, which undermines the effectiveness of those materials since the transmission of SARS-CoV-2 virus is still unknown.\textsuperscript{6} On the other hand, indoor protections are only seen in modern commercial buildings through filtering in central air conditioning which often consume enormous energy due to the use of a pumping system.\textsuperscript{41} Therefore, there is a need to develop high-performance filters with the ability to remove sub-micro and nanoscale particles under non-ideal environments, such as high temperature and high humidity.

1.2 Filter Capture Mechanism and Performance

According to classical filtration theory, there are five capture mechanisms based on the fluid dynamics of a particle with the air stream and the ratio of various forces acting on the particles. The five capture mechanisms by fibrous media include Brownian diffusion, electrostatic interaction, interception, inertial impaction and gravity settling,\textsuperscript{3,13-15,17} shown in Figure 1. During filtration, different mechanisms will dominate different particle size
range. For particles smaller than 0.1µm, random Brownian motion makes particles deviate from the air streamline then collide and deposit on the fibers. Brownian movement becomes more significant with smaller particle size, which makes it the primary capture mechanism for nanoscale particles. When such particles or fibrous media are charged, they will be more firmly adhered due to electrostatic interaction.\textsuperscript{16} For particles in the order of 0.3-10 µm, interception and inertial impaction dominates. If a particle follows the streamline well, it will only intercept with the fibrous media when brought within one particle radius of the fiber. Therefore, interception usually dominates particles from 0.3-1 µm. When a larger particle fails to follow the streamline especially in higher velocities, it will collide directly with the fibers and captured, which is inertial impaction. For particles larger than 10 µm, they are deposited on the fibers due to gravity or trapped between fibers.\textsuperscript{3}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{mechanisms.png}
\caption{Mechanisms of particle capture by fibrous media\textsuperscript{20}. Thick blue lines indicate air flow streamline. Grey circles represent fibers of the filter media.}
\end{figure}

Particles from 0.1-0.3 µm, where no single capture mechanism dominates, usually shows the lowest overall collection efficiency which is often refer to the most penetrating particle size (MPPS)\textsuperscript{3,17,19}. Normally, the MPPS for air filters is about 0.3 µm and its
corresponding filtration efficiency is used to classify air filters. Along with the MPPS, filter performance can also be evaluated by several metrics. Filtration efficiency ($E\%$) is defined as:

$$E\% = 1 - \frac{C_{\text{down}}}{C_{\text{up}}}$$  \hspace{1cm} (Equation 1)

where $C_{\text{up}}$ and $C_{\text{down}}$ are the number of particles counts at filter upstream and downstream, respectively. Fractional penetration ($P\%$), given by $1 - E\%$, is another way to express the percentage of particles that penetrate through the filter. Pressure drop ($\Delta P$) measured across the filter is a crucial factor for efficient filtration. Higher pressure drop indicates that there is a greater resistance for air to pass through the filter which dissipates more energy. Pressure drop ($\Delta P$) is defined as:

$$\Delta P = P_{\text{up}} - P_{\text{down}}$$  \hspace{1cm} (Equation 2)

where $P_{\text{up}}$ and $P_{\text{down}}$ are the pressure measured at filter upstream and downstream, respectively. Quality Factor (QF), which is defined as:

$$QF = \frac{-\ln (1-E\%)}{\Delta P}$$  \hspace{1cm} (Equation 3)

represents the ratio of the filtration efficiency and pressure drop. Filter with lower pressure drop or higher filtration efficiency shows higher QF values which also means better filter overall performance.

1.3 Electrospinning Process

Electrospinning is a simple and well-studied technique for producing randomly-accumulated nano- and micro-scale diameter fibers.\cite{3,21-25} The produced mats show large surface-to-volume ratio and high porosity that are promising for applications ranging from tissue engineering,\cite{26} water purification\cite{27} and wearable electronics.\cite{28} A typical
Electrospinning apparatus is made of three major components: a high voltage supply, a syringe containing polymer solution with a pump and a conductive collector. A basic schematic of the electrospinning apparatus is shown in Figure 2. Electrospinning starts with polymer solution forming pendant drop on the needle that is advanced by a syringe pump with a controllable flow rate. The electrical forces from the applied voltage difference between the needle and the metallic collector overwhelms the polymer surface tension forces that distort the drop into a Taylor Cone. Then, a thin jet of polymer solution ejects from the apex of the Taylor Cone. Instability in the jet under the electric field causes significant bending and whipping, which stretches the jet and the solvent to evaporate. Finally, dry and continuous polymer fibers are deposited on the collector plate.\textsuperscript{21-23}

\textbf{Figure 2.} The schematic of the typical electrospinning apparatus, which composed of a syringe loaded with polymer solution, a high voltage supply and a metallic collector.

One of the main advantages of electrospinning for nanofiber production is the tunable fiber morphology and diameter by specific electrospinning parameters.\textsuperscript{3,21} These parameters can be divided into three categories: Solution, electrospinning process and ambient conditions. For example, by tuning the solution conductivity, solvent volatility, as well as the concentration and viscosity of the polymer solution, one can achieve different
fiber morphologies from the same polymer. To elaborate, when low viscosity precursors are used where there are fewer polymer entanglements with a high number of solvent molecules, surface tension dominates and tend to form beads on the fibers during electrospinning. When the viscosity increases enough to better stretch the solution with solvent molecules evenly distributed among the fibers, smooth morphology is observed. Higher viscosity also tends to form thicker fibers since the solution is harder to stretch. On the other hand, increasing the solution conductivity is a way to decrease the fiber diameter since more charges on the solution can better elongate the fiber. Electrospinning process parameters, including supplied voltage, solution feed rate, type of collector and distance between the needle tip and collector also effects the fiber morphology, but are less dominant than solution properties. For example, smaller feed rate with constant voltage tends to form smaller fiber diameter or beads since less solution is carried by the jet. For ambient conditions such as low humidity will increase the rate of evaporation of the solvent that might clogged up the needle. At high humidity, it is possible that water condenses on the surface of the fiber which eventually create pores on the fibers after drying. Previous studies have demonstrated the ability to synthesize different polymer fibers with smooth surfaces, bead-on-a-string or composite fibers with the fiber diameter ranging from hundreds to several nanometer fibers.29-34

1.4 Electrospun Nanofilters for PM removal

Giving the tunable aspect of the process, previous studies from others have demonstrated great aerosols32-38 and particulate matter removal39-43 using nanofilters with different chemistries and fiber morphologies. For example, Yun et al.33 prepared various fiber morphology structures (uniform fiber, beaded-fiber, composite fiber) from
polyacrylonitrile with diameters ranging from 390 to 420 nm. Matulevicius et al.\textsuperscript{37} compared filtration performance between polyamide, polyvinyl acetate, polyacrylonitrile and cellulose acetate nanofilters. Zhang et al.\textsuperscript{34} was able to fine-tune Nylon 6 fiber size distribution to produce ultrafine nanofibers with diameter smaller than 100 nm.

Another advantage of electrospinning is the ease for post-process treatment including surface functionalization\textsuperscript{31} or plasma treatment\textsuperscript{48} that alter the morphology or chemistry of the nanofibers. Kim et al.\textsuperscript{48} was able to utilized oxygen plasma treatment to generate functional group such as -CONH\textsubscript{2}, -COOH and -COOR on polyacrylonitrile nanofibers which showed higher and stronger PM capture. Coating the fibers with functional chemistries may be an attractive way to modify the fibers to allow a greater amount of surface coverage by designer species rather than burying the species within the fibers.

Adjustments to the electrospinning process have also been published to mass produce the filters\textsuperscript{44,45} and showed outstanding removal efficiency even in non-ideal environment testing, such as high temperature.\textsuperscript{46,47} Xu et al.\textsuperscript{45} utilized a roll-to-roll process to transfer transparent nanofiber films onto plastic mesh that is 10 times faster than direct electrospinning method. Khalid et al.\textsuperscript{44} reported a direct-blow spinning process that is efficient, free of high voltages for large scale coating nanofibers onto window screens for indoor pollution protection.

Several studies have also discussed the structure-property relationships between filter properties and their filtration efficiency.\textsuperscript{49-51} The effect of four common nanofilter physical parameters: fiber diameter, filter thickness (Z), basis weight (W) and packing
density(\(\alpha\)) on the filter performance are often discussed. Basis weight (W) is the filter weight divided by the filter area. Packing density (\(\alpha\)) is defined as:

\[
\alpha = \frac{W}{\rho_f Z}
\]  

(Equation 4)

where \(\rho_f\) is the density of the filter material. Leung et al.\(^{50}\) investigated the relationship between the basis weight, filter thickness, packing density and the filter performance of the electrospun polyethylene oxide fibers. Filtration efficiency were found to be positively associated with basis weight where MPPS decreases with increasing packing density. Wang et al.\(^{32}\) found out by fabricating beads-on poly(lactic acid) nanofilters, the volume fraction of fibrous materials decreases, increasing the permeability of toward air which decreases pressure drop. However, larger pores with lower packing density led to slight decrease in filtration efficiency. Bien et al.\(^{51}\) found that the filtration efficiency is positively associated with filter thickness and negatively associated with fiber diameter for nylon nanofiber. However, there was no clear correlation between packing density and filtration efficiency.

1.5 Objectives of this MS thesis

The goal of this thesis is to improve the overall performance of the electrospun nanofilters, especially removing nanoscale particles. Base nanofiber mats were synthesized from cellulose since it is the most abundant biopolymer\(^{52}\). By controlling the filter thickness, we are able to investigated the relationship between the filter packing density and the overall filter performance. Also, previous literature does not commonly discuss the MPPS; here we investigate this parameter to further evaluate its importance in the ability to removal nanoscale particles using the filters. The first aim of this work is to further
investigate the structure-property relationships of the in-house fabricated cellulose filters, which also optimizing the filters (thickness of layers). The second aim of this work is to investigate how chemical surface modified electrospun nanofiber filters affect air filtration efficiency. Celluloses’ affinity for further chemical modification\textsuperscript{53-55} is another reason why the biopolymer was selected as the base. Polydopamine, was chosen as a bio-glue inspired by mussel adhesive proteins, which forms self-adherent, hydrophilic coatings.\textsuperscript{56-58} Poly(diallyldimethyammounium chloride) (PDADMAC), a polycation, was chosen to compare with the polydopamine coatings. Furthermore, by introducing hydrophilic cellulose and hydrophobic cellulose acetate nanofibers within a composite filter structure, the performance of the composite filter under high humidity environment was also investigated. Overall, this study will show the impact of nanofiber chemistry and packing density on filter performance.

2. Materials and Methods

2.1 Materials and Chemicals

All chemicals were used without further treatment. Cellulose acetate ($M_w = 30000$ Da), dopamine hydrochloride and poly-(diallyldimethylammonium chloride) solution (PDADMAC, 20wt %, $M_w = 100000–200000$ Da) were purchased from Sigma-Aldrich (St. Louis, MO). Tris base, tris hydrochloride, acetone (histological grade), sodium hydroxide (NaOH) and ethanol (absolute anhydrous) were obtained from Fisher Scientific (Fair Lawn, NJ). Mixed Cellulose Ester Deionized (DI) water was obtained from a Barnstead Nanopore Infinity water purification system (Thermo Fisher Scientific, Waltham, MA)
2.2 Fabrication of Cellulose Nanofiber Mat

A 15 w/v% solution of cellulose acetate in acetone was mixed for 24 h at 20 rpm using an Arma-Rotator A-1 (Bethesda, MD). The solution was loaded into a 5mL Luer-Lock tip syringe capped with a Precision Glide 18 gauge needle (Becton, Dickinson & Co. Franklin Lakes, NJ), which was secured to a PHD Ultra syringe pump (Harvard Apparatus, Plymouth, PA). Alligator clips were used to connect the positive anode of a high-voltage supply (Gamma High Voltage Research Inc., Ormond Beach, FL) to the needle and the negative anode to a copper plate wrapped with aluminum foil. A constant feed rate of 3 mL/h, applied voltage of 25 kV, and a separation distance of 10 cm were used to spin cellulose acetate. The assembled electrospinning apparatus was housed in an environmental chamber (CleaTech, Santa Ana, CA) with a desiccant unit (Drierite, Xenia, OH) to maintain a temperature of 22±1°C and a relative humidity of 23%. All nanofiber mats used in this study were electrospun for 30 mins. Cellulose acetate mats were peeled off of the collector plate and sandwiched between two sheets of Teflon to be thermally treated at 208°C for 1 h. For alkaline treatment, cellulose acetate mats were submerged into 0.1 M NaOH solution (4:1 v/v of DI water/ethanol) for 24 h to produce regenerated cellulose nanofibers. All mats were punched into disks with 2.54 cm diameter using a Spearhead 130 Power Punch MAXiset (fluid Sealing Services, Wausau, WI).

2.3 Nanofiber Mat Functionalization

The regenerated cellulose nanofiber mats were functionalized using (i) only polydopamine (PDA) (ii) simultaneous codeposition of PDA and PDADMAC (PDADMAC). Samples were punched into 2.54 cm disks and placed in a 6-well plate with 5 ml of desired functionalization solution and secured to a shaker plate at 150 rpm for 6 h.
For PDA functionalization, the cellulose nanofiber disks were submerged in Tris Buffer (10mM, pH=8.5) containing 2mg/ml dopamine hydrochloride. For PDA/PDADMAC codeposition functionalization, the cellulose nanofiber disks were submerged in Tris buffer (10mM, pH=8.5) containing 2 mg/ml of dopamine hydrochloride and 2mg/ml of PDADMAC. After each treatment, the mats were rinsed with DI water 3 times and placed on Teflon sheets to dry to prevent fiber from adhering to the substrate.

2.4 Materials Characterization

The bulk thickness of each cellulose nanofiber disk was measured at three different locations on each sample using a Mitutoyo 293-330 digital micrometer (Toronto, Ontario, Canada). Micrographs of cellulose nanofiber mats with and without functionalization were obtained using an FEI-Magellan 400 scanning electron microscope (SEM, Hillsboro, OR). The fiber diameter distribution was determined by measuring 50 random fibers from 5 micrographs using ImageJ 1.47 software. A Perkin-Elmer Spectrum 100 Fourier transform infrared spectrometer (FTIR, Waltham, MA) was used to confirm the regeneration and functionalization of the nanofiber mats. High resolution X-ray photoelectron spectroscopy scans were provided by ThermoFisher and were used to determine the chemical composition of functionalized nanofiber mats.

2.5 Particulate Matter (PM) Generation and Filtration Test

PM was generated by burning three incense at a time (Hem Precious Chandan) in a custom-built chamber maintained at a temperature of 22°C. PM particle number concentration and size distribution were measured using a Model 3775 Condensation Particle Counter (CPC) (TSI Incorporated, Shoreview, MN) and a Series 3080 Electrostatic...
Classifier Scanning Mobility Particle Sizer (SMPS) (TSI, Incorporated, Shoreview, MN) at a sample flow rate of 3.0 Lpm. Incense particle concentration was maintained at $2 \times 10^5 \pm 5 \times 10^4$ counts/cm$^3$ and particle size analyzed from 20 to 900 nm. All flow streams were connected by carbonized rubber tubing to reduce loss of charges on the tubing. Single electrospun filters were punched into 2.54 cm disks and stacked-up into 3-layer filters with a total thickness around at 150 or 330 µm. Commercial mixed cellulose ester (MCE) filter membrane discs (47mm) were obtained from Zefon International (Ocala, FL) and used as controls. All filters were tested for 30 mins after connecting the filter module for 10 mins when the incense particle concentrations reached steady state. Pressure drop across the filter was measured before and after filtration using a digital pressure gauge (SSI Technologies, LLC, Janesville, WI) in line with a vacuum pump maintained at a face velocity of 15.1 cm/s using a size number 4 metal critical orifice (O’Keefe Controls Co., Trumbull, CT).

3. Results and Discussions

3.1 Characteristics of Cellulose and Functionalized Nanofiber Filters

Cellulose nanofiber mats were successfully regenerated from electrospun cellulose acetate nanofibers via alkaline treatment, which served as the base materials for the two surface functionalization treatments examined. FT-IR spectra for as-spun cellulose acetate, regenerated cellulose, and cellulose functionalized with PDA or PDADMAC are presented in Figure 3. Notably, the disappearance of the 1750 cm$^{-1}$ peak for cellulose nanofilter after alkaline treatment indicates that the acetate groups have been replaced with hydroxyl groups, supporting the success regeneration from cellulose acetate. The peaks found on
PDA and PDADMAC functionalized samples around 1250 cm\(^{-1}\) and 1500 cm\(^{-1}\) indicates the presence of aromatic rings from the deposition of polydopamine.\(^{59-60}\)

![FT-IR spectra](image)

**Figure 3.** FT-IR spectra for as-spun cellulose acetate, regenerated cellulose, and cellulose functionalized with PDA and PDADMAC nanofilters.

To further confirm the successful coating of polydopamine and PDADMAC on cellulose nanofilters, elemental data analysis via representative survey scans and high resolution XPS for carbon, oxygen and nitrogen were obtained, **Figure 4.** XPS narrow-scan analysis of the N\(_{1s}\) showed a signal at 399 eV for both functionalized nanofilters but not found on the bare cellulose nanofilter, which represents the presence of polydopamine, since the 399 eV signal was contributed from the primary amine group.\(^{61}\) Another N\(_{1s}\) signal around 402 eV showed in **Figure 4(c)** indicated the present of the positively charged nitrogen atoms on PDADMAC, which distinguished the two functionalized samples we synthesized.\(^{59}\) Elemental analysis data is summarized in **Table 1.**
Scanning electron microscopy (SEM) was utilized to analyze the structural morphology and the fiber diameter distribution for each electrospun nanofilter, displayed in Figure 5. These images showed that all filters exhibit great fiber interconnectivity at the same time with pores larger than fiber diameter which were randomly distributed over the

Table 1. Summary of the elemental data analysis of the high resolution XPS that provides surface chemical composition analysis of cellulose, PDA and PDADMAC electropun nanofilters.

<table>
<thead>
<tr>
<th>Nanofilters</th>
<th>C (%)</th>
<th>O (%)</th>
<th>N (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cellulose</td>
<td>59.1</td>
<td>38.6</td>
<td>0.1</td>
</tr>
<tr>
<td>PDA</td>
<td>64.0</td>
<td>33.4</td>
<td>2.5</td>
</tr>
<tr>
<td>PDADMAC</td>
<td>65.8</td>
<td>31.5</td>
<td>1.5</td>
</tr>
</tbody>
</table>

Figure 4. XPS spectra of (a) survey scans including cellulose, PDA and PDADMAC nanofilters and high-resolution scan of N1s for (b) PDA (c) PDADMAC nanofilters as a function of binding energy (eV).

Scanning electron microscopy (SEM) was utilized to analyze the structural morphology and the fiber diameter distribution for each electrospun nanofilter, displayed in Figure 5. These images showed that all filters exhibit great fiber interconnectivity at the same time with pores larger than fiber diameter which were randomly distributed over the
filters allowing air stream to pass through. The pore size of the cellulose nanofilter is estimated to be around 4-8 µm based on previous studies,\textsuperscript{24,62} which means it does not remove particle trapping or sieving since the size of the incense particles investigated are in the submicron and nanoscale range. The specific surface area is estimated to be 4.5 m$^2$/g based on previous work.\textsuperscript{26,62} Regenerated cellulose nanofibers in Figure 5(a) showed smooth and fibrous morphology with an average fiber diameter of 0.9 ± 0.3 µm, consistent with previous reports. PDA coated nanofibers showed rough morphology with particles aggregated throughout the fibers, thus giving a larger fiber diameter at 1.4 ± 0.4 µm, which is consistent with previous works. Particle aggregation was eliminated for PDADMAC codeposited fibers, showing smooth morphology and larger fiber diameter as well as fiber distribution (1.7 ± 07 µm). Notably, previous work using a one-step codeposition of the polymer zwitterion, poly(2-methacryloyloxyethyl phosphorylcholine) and polydopamine also showed reduced polydopamine particle aggregation. Overall, the average fiber diameter of functionalized fibers remained equivalent to the bare cellulose nanofilter. SEM images of mixed cellulose ester control filter is shown in Figure 5(d). MCE control filter is composed of crystalline structure of cellulose acetate and nitrocellulose, where the filter pore size is around 0.8, as reported by the manufacturer.
Figure 5. SEM images and fiber diameter distribution for (a) bare cellulose (b) 2 mg/ml PDA and (c) 2 mg/PDA + 2 mg/ml PDADMAC codeposited electrospun nanofiber mats (d) Mixed cellulose ester (MCE) control filter. Fiber diameter distribution display average fiber diameters and standard deviation.
3.2 Filtration Performance vs Nanofiber Packing Density

Figure 6. (a) Schematic diagram of single and multilayer electrospun nanofilters with different thickness. (b) Packing density as a function of total thickness for all cellulose nanofilters investigated in this work. (c) Fractional penetration as a function of particle electrical mobility diameter ranging from 20 to 400 nm for each single layer and multilayer nanofilters. Overall filtration efficiency is displayed in the upright corner.

Figure 6(b) summarizes the packing density of all the cellulose nanofilters investigated in this work. Filters were electrospun under the same condition and with the total thickness chosen around 150 or 330 µm to compare with control filter which is 150 µm thick. Giving the nonuniformity nature of electrospinning process, the packing density of the filters varied even with similar thickness. Individual filter performance was investigated to compare with the multilayer filters, where the particle fractional penetration is showed in Figure 6(c). Notably, the multilayer filter showed higher removal efficiency, and also displayed the highest particle selectivity for particle sizes over 50 nm. The benefit of stacking up multiple filters was illustrated in previous work\textsuperscript{50}, showing improvement in filtration efficiency but not altering the quality factor, which is in accordance with our results. Therefore, 3-layer nanofilters were tested and investigated throughout the remainder this work.
The relationship between packing density with filtration efficiency, pressure drop and quality factor is summarized in Figure 7. Notably, filtration efficiency is negatively associated with packing density within the same filter thickness. In recent work by others, filtration efficiency was found to be greater for thicker mats with higher packing densities.\textsuperscript{49-51} A possible explanation for the trend is less packed filters exhibit a greater effective surface area available for particle capture by diffusion and interception. On the other hand, pressure drop is positively associated, while quality factor is negatively associated with packing density regardless of the filter thickness. Based on theoretical calculations,\textsuperscript{50} pressure drop increases with packing density meaning greater resistance for air to penetrate. Most of the thicker mats outperform the control filters with higher quality factor. In conclusion, greater filter performance can be achieved by electrospinning filter with lower packing density.

![Figure 7](image)

**Figure 7.** (a) Filtration efficiency (b) Pressure drop and (c) Quality factor as a function of packing density for control, and cellulose nanofilter samples. Samples having total filter thickness around 330 and 150 µm are listed.

Functionalized cellulose nanofilters including PDA and PDADMAC with a total thickness around 330 µm were also investigated, results are summarized in Figure 8. Filtration efficiency and quality factor were again found to be negatively associated with
quality factor, where pressure drop was positively associated. Meaning that the overall filter performance is dictated by the nature of the electrospun cellulose filters, and the effect of functionalization was subtle based on such characteristics. Notice that the pressure drops still remain in the range around 140 to 180 Pa even after functionalization, indicating minimum structural difference between bare and functionalized cellulose nanofilters. Several functionalized filters with Quality factor above 0.03 Pa\(^1\), shown in Figure 8(c), exhibit a sign of overall filtration performance improvement.

![Figure 8](image)

**Figure 8.** (a) Filtration efficiency (b) Pressure drop and (c) Quality factor as a function of packing density for control, PDA and PDADMAC samples. All samples having total filter thickness around 330 µm.

### 3.3 Selectivity and Particle Penetration of Nanofilters

To further investigate the particle size selectivity of the nanofilters and MCE control filter, penetrated particles were analyzed using a scanning mobility particle sizer (SMPS) over a range of 20 to 900 nm. Notice that only nanofiber filters with over 98.5% overall filtration efficiency were displayed in Figure 9. Figure 9(a) shows the distribution of the upstream incense particles and the downstream particles collected by the SMPS. The MPPS for control, cellulose, PDA and PDADMAC is around 162.5, 140.7, 168.5 and 174.7 nm, respectively. As suggested by the literature\(^{19,50}\) MPPS decreases with decreasing fiber
diameter which is accordance with our results, since the average fiber diameter for cellulose, PDA and PDADMAC are 0.9, 1.4 and 1.7 µm. Fractional penetration for different particle size was further calculated based on the upstream and downstream particles, which are displayed in Figure 9(b) and (c). The overall filtration efficiency for each sample is displayed in the right corner and the fractional penetration is plotted in the range of 0 to 40%. Only particle smaller than 200 nm was shown in Figure 9(b), since at least 98% fractional removal was achieved for particle size larger than 200 nm for cellulose, PDA and PDADMAC samples. Notice that the nanofilters demonstrated much superior ability to remove particles larger than 70 nm compared to the control filter. Since the nanofiber and control filters have similar chemical composition, the fiber interconnectivity of the nanofiber filters is what distinguishes them from the control commercial filter. From Figure 9(c), particles around 41.9 nm showed the highest fractional penetration at 19.0, 34.7, 5.26 and 2.32% for control, cellulose, PDA and PDADMAC, respectively. Since the capture of nanoparticles is mainly dominated by diffusion and electrostatic interactions, the fiber diameter difference between these samples had only a subtle effect on it. The additional functional group on PDA and positively charged PDADMAC coatings greatly improved the capture of particles from 30 to 60 nm compared to bare cellulose nanofiber mats. Overall, PDADMAC nanofilters demonstrated the best particle penetration resistance for all particle size among all samples.
Figure 9. (a) Normalized particle size distribution for incense particles (upstream) and downstream particles for control, cellulose, PDA and PDADMAC nanofilters. (b) Summary of filtration efficiency (E%), pressure drop, quality factor and fractional penetration percent (P%) for 41.9 nm particle for Control, Cellulose, PDA, PDADMAC samples. Fractional penetration as a function of particle electrical mobility diameter ranging (c) from 20 to 200 nm and (d) from 20 to 100 nm for control, cellulose, PDA and PDADMAC nanofilters. Overall filtration efficiency is displayed in the upright corner.
3.4 Long-Term and High-Humidity Nanofilter Performance

The long-term performance of the cellulose nanofilters was also investigated. Filtration experiments were conducted for four cycles, 20 mins for each cycle. After 80 mins of filtration, the pressure drop increased by only 5% and a slight increase in filtration efficiency was observed. The particle fractional penetration for each cycle is displayed in Figure 10(a). The highest particle fractional penetration percent and filtration efficiency for each cycle is 27.9, 12.5, 43.1, 17.9 % and 97.0, 99.0, 99.0, 98.2%, respectively. The abrupt increase MPPS penetration in the 3rd cycle is still unknown. Since the pores will become blocked for even longer tests, filtration efficiency and pressure drop are both expected to increase. SEM images of cellulose nanofilters after 20 and 80 mins of filtration are displayed in Figure 10 (b) and (c), respectively. There are more particles observed and deposited on the fibers after 80 mins of filtration, but the pores are still available (i.e., not clogged). In conclusion, our cellulose nanofilters will still perform effectively after 80 mins of usage.
When moisture obstructed the pores on the filters, not only is the filtration efficiency reduced due to the dissipation of the charges on the fibers, but the thermal-physiological comfort is also decreased, which is important if the filters were utilized in personal protection masks. To improve the applicability of the filters in high humidity environment, Zhao et al.\textsuperscript{1}\textbf{1} proposed a composite super-hydrophilic/hydrophobic gradient structure that increases the moisture-vapor transmission rate (MVTR), which also offered an easy-to-clean property. Hydrophilic nanofiber exhibits high water adsorption and diffusion rate but tends to form capillary water films that increase air resistance dramatically over time under high humidity. On the other hand, hydrophobic nanofibers have low MVTR and thus, result in poor thermal-physiological comfort. To incorporate the two distinct wetting properties, super-hydrophilic poly-acrylonitrile/silicon-dioxide

\textbf{Figure 10.} (a) Particle fractional penetration percent and filtration efficiency of cellulose nanofilters for each cycle of filtration. SEM images of cellulose nanofilters after (b) 20 and (c) 80 mins of filtration.
fibers and hydrophobic polyvinylidene fluoride fibers were layered to enhance the driving force of the moisture transmission rate at the same time prevent capillary water film from filming.

Using the same idea, we were able to fabricate a gradient filter structure using hydrophilic cellulose and hydrophobic cellulose acetate nanofilters. A layer of hydrophobic cellulose acetate filter was layered under a 3-layered cellulose filter to form a composite filter, the schematic of composite as well as hydrophilic and hydrophobic filters is displayed in Figure 11(b). Contact angle measurement results were shown in Figure 11(c). Notice that water drop was immediately adsorbed on cellulose nanofilter which indicates its total-wetting property, where cellulose acetate exhibited a non-wetting property with a contact angle at 145°. The results of cellulose, cellulose acetate and composite filters were tested under 70% relative humidity environment, results are shown in Figure 11(a). Large amount of incense particles penetrated the cellulose nanofilters along with water droplets, giving only 81.4% of filtration efficiency and a pressure drop of 27.6 Pa. Meaning that the capillary film makes the hydrophilic filter much more penetrable for both incense and water particles at the same time decreases the air resistance of the filter. By introducing the composite structure, the filtration efficiency was dramatically increased to 98.9% with a pressure drop at 158 Pa, which mean the filter performance was compatible with filtration conducting in low humidity. SEM images of cellulose nanofilters after testing in high humidity environment are displayed in Figure 11(d), where the fiber morphology remains unchanged and incense particles were again observed as being trapped within the filter.
Figure 11. (a) Fractional penetration as a function of particle size ranging from 20 to 900 nm. (b) Schematic diagram of cellulose, cellulose acetate and composite gradient filter structure. (c) Contact angle measurements results for cellulose and cellulose acetate nanofilters. (d) SEM images of cellulose nanofilters after high-humidity test.
4. Conclusion

By manufacturing electrospun nanofilters with similar thicknesses, we were able to investigate the relationship between filter packing density and filter performance (filtration efficiency, pressure drop, quality factor). Furthermore, by layering the nanofibers, the filtration efficiency for particle size larger than 50 nm was greatly improved. Filtration efficiency and quality factor were found to be negatively associated with packing density under similar filter thickness, where pressure drop was positively associated. Successful surface chemistry modification by deposition of the bio-inspired glue PDA and polycation PDADMAC greatly improved the removal of nanoparticles smaller than 50 nm, where the particle fractional percent for particle size at 41.9 nm was decreased from 34.7 to 2.32%. After 80 mins of filtration under very high particle concentration, pressure drop only increased 5% for cellulose nanofilters where filtration efficiency slightly increased. Finally, by introducing hydrophilic/hydrophobic gradient filter structure, composite filter structure was able to remove 98.5% of water and incense particles under 70% relative humidity environment. In conclusion, surface functionalized cationic cellulose nanofilters were able to remove at least 99% of particles smaller than 40 nm. Also, by introducing hydrophilic/hydrophobic composite structure, the filtration performance remains even under 70% relative humidity.
5. References


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