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# Enhanced Capture of Particulate Matter by Molecularly Charged Electrospun Nanofibers

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**ABSTRACT:** We introduce molecularly charged electrospun nanofibers obtained by soft chemical treatment for the capture of particulate matter (PM). These PMs, along with certain volatile organic compounds (VOCs), pose a severe threat not only to human health but also to the environment. As the concentrations of these PMs have been steadily increasing in the Southeast Asian countries, a dire need for protection against these particles is warranted. Filtering out the polluted air using various filtration media, such as face masks and nasal filters, has been the standard method for minimizing exposure to PM. Here, we demonstrate the removal of PM and VOCs by utilizing electrospun nanofibers of polystyrene (PS) and polyacrylonitrile (PAN) with molecular charges imparted on them via chemical treatment. The chemically treated fibers were successful in capturing even particles measuring 300 nm, which are considered to be the most penetrable particles. We report a filtration efficiency of ~93% for removing such particles, which is ~3 ± 1.5% enhancement when compared to the untreated fibers. The fibers have been subjected to extreme haze conditions (~1413  $\mu$ g m<sup>-3</sup>) of PM<sub>2.5</sub> for a duration of 1 h, and the filtration efficiency was measured to be ~99.01%. These fibers also possess the capability to capture model VOCs such as aniline, toluene, tetrahydrofuran, and chloroform. When PAN, PS, and their chemically treated counterparts were tested for their antibacterial activity, these filter mats had bactericidal effect on *Escherichia coli, Bacillus subtilis*, and *Enterococcus faecalis*. A nasal plug hosting these filter mats has been designed, which can offer personal protection from PM. Enhanced removal of residual particles is extremely important, and this difficult task is made possible with our approach. The efficiency of our approach is due to the charged nature of PM, especially of the smaller size regime.

**KEYWORDS:** electrospun fibers, particulate matter, volatile organic compounds, nasal filters

# INTRODUCTION

An exponential rise in air pollution and its consequences for human health and environment have raised serious concerns, warranting appropriate solutions for remediation. Natural phenomena such as dust storms, volcanic eruptions, forest fires, sea droplet impact on surfaces, <sup>1–3</sup> and man-made sources such as combustion of fossil fuels, agricultural waste, and vehicular emissions are some of the causes for the rise of particulate matter (PM) in air. Polluted air primarily comprises solid particles suspended in air, called PM, and volatile organic compounds (VOCs). These PMs are composed of both organic and inorganic (SO<sub>x</sub>, NO<sub>x</sub>, F<sup>-</sup>)<sup>4,5</sup> species, minerals (such as calcite, dolomite, anorthite, and feldspar),<sup>6,7</sup> and soil dust. Solid particles with diameters,  $d < 2.5 \ \mu m \ (PM_{2.5})$  and <10  $\ \mu m \ (PM_{10})$ , are of prime importance as they can enter lungs,<sup>8</sup> and their prolonged exposure can even cause cancer.<sup>9–11</sup> Adverse health effects pertaining to VOCs are well known: headaches and nausea, damage to the central nervous system, kidney, lung, and liver.<sup>12</sup> Extended exposure to

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high levels of pollution can severely affect the very young and elderly. There is a rise in polluted air in the recent past in different parts of India and other developing nations of Southeast Asia. Rise in PM causes prolonged hazy days, and visibility is highly compromised. Extended deposition of dust can also severely affect the performance of solar panels, among other things.

Utilizing a centralized ventilation system to achieve a controlled indoor environment is the only means of protection against polluted air. Ventilation systems offer high efficiency in removing PM but consume high energy in generating clean air.<sup>13</sup> Use of commercial-grade filter masks as a primary means of protection against PM has been the standard practice. However, many commercial masks provide negligible efficiency for filtering PM<sub>10</sub> and PM<sub>2.5</sub>; in addition, they offer resistance to airflow.<sup>14</sup> PMs are generally captured by impact, interaction, or diffusion of particles on the fiber surface because of their varied chemical, physical, and mechanical properties. Ideally, a good filter needs to remove the maximum amount of PM<sub>25</sub> while offering minimum resistance to airflow and also providing high mechanical stability. Electrospinning is one of the versatile routes by which such filter mats can be fabricated. Recently, Cui et al. have made electrospun fibers out of polyacrylonitrile (PAN), polystyrene (PS), polyvinyl pyrolidone, and polyvinyl alcohol (PVA), which show high efficiency (above 98%) in filtering  $PM_{2.5}$ .<sup>15</sup> By modifying the surface morphology and increasing the hydrophilicity of PAN, Jing et al. showed a better filtration of soot.<sup>16</sup> Li et al. recently fabricated polytetrafluoroethylene/(PVA) electrospun fibers, and after removing PVA, the resulting fibers had a filtration efficiency of 98.05% for filtering  $PM_{2.5}^{17}$  Substrates made of textiles have gained significant attention for capturing PM, which is due to their flexibility, minimum resistance to airflow, and low manufacturing cost.<sup>18</sup> Forming hierarchical structures on these electrospun fibers has found multiple applications in air and water purification.<sup>19-21</sup> Huang et al. fabricated hierarchical structures on polycaprolactone/polyethylene oxide nanofibers by exposing the electrospun mat to acetone vapors, which caused physical wrinkles on these fibers creating hierarchical structures, and these modified fibers had a clear  $\sim$ 20% rise in their particulate removal efficiency.<sup>22</sup> These, coupled with the possibility of functionalization by metalorganic frameworks (MOFs), show potential as a washable and reusable medium for capturing soot.<sup>23</sup> However, because of the brittle nature of MOFs, the interactions between MOF and the textile substrate need further attention as they could have poor adhesion and may not be suitable as a personal filter mask. A disposable gelatin electrospun fiber-based multifunctional air filter was fabricated by Souzandeh et al., where the paper towel was used as a substrate to collect these gelatin nanofibers.<sup>24</sup> Other eco-friendly materials such as cellulose nanocrystals,<sup>25</sup> wood pulp,<sup>26</sup> and lignin<sup>27</sup>-based air filters were fabricated and used for obtaining clean air devoid of PM. Apart from PM<sub>10</sub> and PM2.5, particles with size <300 nm (PM0.3) are generally not captured by common masks, and these are considered to be highly penetrating airborne particles having dire con-sequences on health.<sup>28</sup> In an urban environment, traffic emissions are considered to be a major source for ultrafine particles.<sup>29</sup> During the combustion of fuels, ion concentrations are generated, wherein the nucleation of ultrafine particles occurs.<sup>30</sup> Because of the ion-particle collision, these particles attain charges, either positive or negative. Charges on these particles greatly affect the coagulation and transport.

Coagulation leads to increase in the particle size, which causes changes to the aggregate geometry and further modifies the diffusion coefficients.<sup>31</sup> For the capture of these extremely small particles, Wang et al. investigated an electret-type nanofiber based on triboelectric nanogenerators obtained from electrospun polyimide and polyvinylidene fluoride (PVDF).<sup>32</sup> PM<sub>0.3</sub> is considered to be the most penetrable particle, and commercial-grade masks cannot capture them.<sup>33</sup> Recently, Li et al. fabricated an anionic surfactant Steiner geometry-based electrospun PVDF fiber for capturing these 300 nm PMs.<sup>34</sup> Parameters such as lower pressure drop, flexibility, high filtration efficiency, and affordability need to be addressed in defining an ideal filter medium.

VOCs constitute a major component of both indoor and outdoor pollutants, the former being a major concern for children.35 Some of the common health effects are asthma, allergies, and chronic obstructive pulmonary disease, which is primarily caused by increased indoor air pollutants.<sup>36,37</sup> Prolonged exposure to VOCs such as benzene, toluene, xylene, and so forth can lead to cancer. In view of these concerns, developing appropriate materials capable of adsorbing these VOCs is necessary. Usually, activated carbon has been used for the removal of VOCs because of its large surface area and pore volume. However, major limitations are due to high-pressure drop across the bed, minimal mechanical flexibility, and faster saturation. Recent reports suggest that electrospun fibers are capable of adsorbing VOCs and also offer additional features such as flexibility and minimum pressure drop.<sup>38</sup> Scholten et al. demonstrated the capability of electrospun polyurethane fibers for adsorbing VOCs.<sup>39</sup> These fibers show an affinity for adsorbing toluene and chloroform and limited affinity toward hexane.

In this work, we have fabricated a chemically charged filter mat that can be used in diverse situations to filter both PM and VOCs. This mat consists of electrospun PAN and PS fibers that have been chemically treated to increase the surface charge, both negative and positive, which, in turn, improved the filtration efficiency of  $PM_{0.3}$  by ~3 ± 1.5%. In addition, this filter mat was capable of removing model VOCs such as toluene, tetrahydrofuran (THF), aniline, and chloroform. The mat offers a reduced resistance of <60 Pa to airflow. These filters were also effective in filtering under extreme haze conditions (~1416  $\mu$ g m<sup>-3</sup>) of constant exposure to PM<sub>2.5</sub> when continuously used for 24 h. The fiber mats were also tested for their antibacterial property using Gram-negative bacteria Escherichia coli and Gram-positive bacteria Bacillus subtilis. In addition, they were also tested on Enterococcus faecalis, a pathogenic bacterium commonly found in root canal and saliva. Investigation on E. faecalis found in saliva revealed that they possess the highest abundance of virulence genes when compared to the isolates from other parts of the body.<sup>40-42</sup> They are also known to cause nosocomial infections.<sup>43</sup> A nasal plug designed to host this filter mat can serve as a personal protective gear with minimal inconvenience for daily use.

## EXPERIMENTAL METHODS

**Materials.** Commercial-grade PAN and general-purpose PS were purchased from Sandhya Polymer Industries, India, and Vardhaman Acrylics Ltd., India, respectively. Dimethylformamide (DMF), sulfuric acid (H<sub>2</sub>SO<sub>4</sub>), acetonitrile (ACN, HPLC grade), and hydrochloride acid (HCl) were purchased from Sigma-Aldrich. Choline chloride (referred to as ChCl throughout the article), aniline, toluene, ethanol,

chloroform, and THF were purchased from RANKEM, India. Fumed silica particles were purchased from Astra Chemicals, India. Milliporeprocessed deionized water (~18.2 M $\Omega$ ) was used throughout the experiments, and all chemicals were used without further purification. Nutrient agar, *E. coli* MTCC 739, and *B. subtilis* ATCC 21331 were procured from MTCC and ATCC, respectively. *B. subtilis* (ATCC 21331) was provided by Prof. S. Gummadi (Department of Biotechnology, IITM). *E. faecalis* was obtained as a gift from Dr. A. R. Pradeep Kumar, Thai Moogambigai Dental College and Hospital, Chennai, India.

**Methods.** Preparation of Electrospun Fibers. About 2 g (20 wt %) of PS and 1.4 g (14 wt %) of PAN were dissolved separately in 10 mL of DMF. These two were stirred for 6 h in ambient conditions to obtain uniform solutions. Later, they were loaded into disposable syringes with a flattened 21G needle. The PAN and PS nanofibers were prepared separately using the ESPIN-NANO electrospinning machine. The spinning parameters for PAN were as follows: a flow rate of 0.5 mL h<sup>-1</sup>, a working distance of 14 cm, and a voltage of 15 kV, applied for a period of 30 min. For PS, a flow rate of 1 mL h<sup>-1</sup>, a working distance of 14 cm, and a voltage applied for a period of 30 min were used. These fibers were collected on a nonwoven (NW) polypropylene (PP) mat placed on a rotating drum collector.

Imparting Surface Charges on the Fibers. To impart positive charge on the fibers, about 0.6 g of PAN fibers was immersed in 0.1 M HCl solution containing an optimized concentration of 216 mM ChCl. This solution, along with fibers, was left undisturbed for 30 min. Later, these fibers were rinsed with deionized (DI) water repeatedly and finally dried overnight in an oven at 60 °C. This treatment anchors positive charges on PAN fibers. Similarly, PS fibers were immersed in 3 M  $H_2SO_4$  solution at room temperature for 24 h.<sup>44</sup> Finally, these sulfonated PS (SPS) fibers were rinsed repeatedly to remove the unbound acid moieties and dried overnight in an oven at 60 °C.

Assembly of the Filtration Mat. A NW PP mat was cut into dimensions of  $13 \times 16$  cm and placed on a drum collector and used as a substrate for collecting PAN and PS fibers. Subsequently, PAN and PS fibers were placed on top of each other, and the combined fibers were later placed between two NW PP mats, forming the entire filter mat. A similar protocol was followed for the chemically treated counterparts. These PP mats provide structural stability but have negligible efficiency for filtering PM<sub>10</sub>, PM<sub>2.5</sub>, and VOCs.

Filtration Efficiency of the Fiber Mat. To determine the filtration efficiency of the fiber mat, we fabricated an aerosol filtration efficiency tester (AFET) based on the ASTM F2299 protocol.<sup>45</sup> Briefly, clean compressed air was obtained from a compressor coupled with a highefficiency particulate air filter. This compressed-air was split into two streams, with one being used to aerosolize the aqueous NaCl solution and the other being directed to the dilution chamber. These two streams were then combined in the dilution chamber to reduce the concentration of NaCl aerosols, which pass through an 80 cm long cylindrical tube with a face velocity of 5 cm  $s^{-1}$  and a flow rate of 16 L min<sup>-1</sup>. The pressure drop across the filter was measured using a differential pressure gauge. The input and output aerosol concentrations were measured using a laser particle counter (Lasair III, Particle Measuring System), and the filtration efficiency was calculated. Commercial-grade fumed silica powder was used as model solid aerosols, and their capture was also studied. The filter mat considered for this test had an area of 10 cm<sup>2</sup>. A schematic of the AFET setup is shown in Figure S1. Extreme haze conditions were simulated by using soot obtained from the burning of incense sticks, and an optical image of the experimental setup is shown in Figure S2. The filters were placed between two glass bottles, and soot was introduced into the left chamber. The concentrations of aerosols in the left chamber and the right chamber were counted using a particle counter (Perfect Prime AQ9600). For measuring the efficiency of these filter mats at prolonged exposure to PM, fresh soot was introduced at the end of every hour, and the particulate concentrations were measured for the same sample. The size of the filter sample was 4 cm<sup>2</sup> for testing the soot removal efficiency. A

digital manometer (HTC instrument PM-6105) was used to measure the pressure drop across the mat before and after filtration. The pressure drop was calculated under two flow rates, 5 and 8 L min<sup>-1</sup> using the IPM-191 dust collector. The filtration efficiency was calculated based on the equation of filtration efficiency ( $\eta$ ) = ( $C_0 - C$ )/ $C_0 \times 100$ , where  $C_0$  and C are the PM concentrations without and with a filter mat, respectively. The performance of the filter mats was quantified using a quality factor (QF), where QF is the ratio of penetration of particles (1 –  $\eta$ ) to the pressure drop ( $\Delta P$ ) across the

filter,  $(QF) = -\ln(1 - \eta)/\Delta P$ . Dust Sampling and Processing. Dust settled on leaves was collected from four residential locations within the campus of Indian Institute of Technology Madras. These particles were collected by scooping them using a nylon-bristled soft brush and storing within a polyethylene bag. The particles were ground using a mortar and pestle and sieved to <100  $\mu$ m. About 500 mg of these particles was dispersed in ethanol, sonicated, and centrifuged thrice for 10 min at 5000 rpm.<sup>46</sup> These particles, after multiple washing, were dried overnight at 70 °C and stored in vials for charge and X-ray diffraction (XRD) analysis. Furthermore, indoor dust was collected onto a 25 mm cellulose filter paper with a pore size of 0.22  $\mu$ m using a dust collector (IMP-191, INSTRUMEX) for 8 h, with a flow rate of 9 L min<sup>-1</sup>. The dust was collected consecutively for 20 days, and the filter paper was backwashed using DI water and stored.

Uptake of VOCs by the Fiber Mat. Using chloroform, aniline, THF, and toluene as model VOCs, their uptake by electrospun fibers was studied. Briefly, electrospun mats of 2, 10, and 20 mg were placed at the bottom of a glass desiccator containing a beaker with 40  $\mu$ L of the intended VOC. The desiccator utilized was 30 cm in diameter and height. After exposing the fibers for 1 h, the sample was removed and placed inside a hood for 30 min to remove any excess/unadsorbed VOC. This sample was then immersed in a beaker containing 4 mL of ACN for 2 h. Finally, 0.5 mL of this solution was loaded into high-performance liquid chromatography (HPLC) vials, and chromatography was performed.

Antibacterial Activity Tests. The fibers were tested for their antibacterial activity through the zone inhibition method against Gram-negative bacteria *E. coli* and Gram-positive bacteria *B. subtilis* and *E. faecalis*. Fibers of PAN, PP, PS, ChCIPAN, and SPS were cut to dimensions of  $\sim 10 \times 10$  mm and placed gently on the nutrient agar plates inoculated with *E. coli*, *B. subtilis*, and *E. faecalis* using the uniform streaking method. The plates were incubated overnight at 37 °C for 24 h, and the bacteria growth inhibition zone around the fiber mats was observed.

Characterization. For determining the fiber diameter and morphology, the mats were analyzed using an FEI QUANTA 200 scanning electron microscope coupled with an energy-dispersive spectroscope. The samples were sputtered with gold using a CRESSINGTON sputter-coater. For the confirmation of surface functionalization, the fiber mat was made into a pellet using KBr as the matrix and analyzed using PerkinElmer Spectrum One FTIR. XRD studies for the samples were performed using a Bruker D8 ADVANCE powder X-ray diffractomer. Contact angle measurements were performed using a sessile water droplet of volume 3  $\mu$ L using a Holmarc contact angle meter. Finally, a Shimadzu Prominence Analytical high-performance liquid chromatograph equipped with a photodiode array detector was used to measure the VOC uptake capacity. An injection volume of 5  $\mu$ L on the C18 column with a flow rate of 0.5 mL min<sup>-1</sup> with ACN (100%) as the mobile phase was chosen.

# RESULTS AND DISCUSSION

Active and Passive Monitoring of Dust. To determine the physical and chemical nature of dust, ambient dust was captured actively and passively. Indoor dust was collected onto a cellulose-based filter paper using a dust collector, IPM-191. The filter paper, upon washing with DI water, released the trapped particles into the solution, which was then stored in centrifuge vials. This suspension was analyzed to determine the

To determine the size of the passively monitored dust, particles deposited on leaves were analyzed using a scanning electron microscope. Typically, the leaves were at a height of  $\sim$ 6 m from the ground. Micrographs of the dust are shown in Figure S4c,d. The particles were highly irregular and nonuniform. A Faraday cup coupled to a Keithley 6514 electrometer was used to determine their charge in the native environment. The system was stabilized for 300 s, after which about 500 mg of the collected particles was added to it. Upon addition, a steep increase in charge was observed, and the cumulative charge of the particles was  $1.4 \times 10^{-10} \ \mu$ C, which was stabilized to  $1.0 \times 10^{-10} \,\mu\text{C}$ , as shown in Figure S4a. A similar experiment was performed using particles from another location, and the cumulative charge was found to be  $-2.0 \times$  $10^{-8} \mu$ C, as shown in Figure S4b. To determine the chemical nature of the dust, XRD analysis of the passively collected samples was performed. Diffraction patterns of the dust samples from four different locations are shown in Figure S5. They were compared with the Inorganic Crystal Structure Database (ICSD) using the X'pert High Score Plus to characterize the composition. The samples were seen to predominantly contain mixtures of quartz and albite, both  $\alpha$ and  $\beta$  forms, in agreement with previous reports.<sup>47</sup> <sup>49</sup> The chemical compositions of the minerals that matched with the dust collected from four different locations are shown in Table S1.

Electrospun Fiber Mats for the Capture of PM. To efficiently capture PM and VOCs, electrospun fibers of PAN and PS were chosen. These fibers were chemically treated to impart molecular charges on them so as to enhance the filtration efficiency. Owing to its versatility, electrospinning technique was chosen for the fabrication of these polymeric nanofibers. Briefly, it is a technique wherein a high voltage of 15 kV is applied to a syringe containing a polymeric solution. This electrical force overcomes the surface tension of the solution and draws the solution as fibers.<sup>50,51</sup> These fibers can be collected either on a metal plate or on a NW fiber mat or glass. We chose a NW mat, as shown in Figure 1. A molecular model of ChCl-treated PAN is also shown in Figure 1. The calculated dipole moments of untreated PAN and PS were 3.9 D and 0.29 D, respectively, and after chemically treating these fibers, the dipole moment increased to 11 D for choline-treated PAN and 13.86 D for SPS. For this, the structure was initially drawn in Avogadro, and for density functional theory (DFT), we used the B3LYP method with a 6-31G(d) basis set. After initial structure optimization, the coordinates were exported to Gaussian 09 for complete optimization of the structure to obtain the dipole moment,<sup>52</sup> The dipole moment was calculated using the expression  $\mu_{\text{total}} = (\mu_x^2 + \mu_y^2 + \mu_z^2)^{1/2}$ , and the corresponding coordinate file is attached in the Supporting Information. In the present study, PM was generated by three methods: (1) aerosolizing aqueous NaCl droplets (size range of 300 nm to 3  $\mu$ m), (2) burning an incense stick (sizes of 2.5 and 10  $\mu$ m), and (3) fluidizing fumed silica (size range of  $1-30 \ \mu m$ ). We chose aniline, THF, toluene, and chloroform as representative model VOCs present in air, and their uptake by the fibers was studied.



**Figure 1.** (Top left) Schematic representation of the electrospinning technique; fibers were collected on a NW fiber mat placed on a drum collector. These fibers captured PM to provide clean air. (Top right) Enlarged image illustrating the capture of particles because of the positive charge on the fibers. (Centre) Further enlargement to illustrate the molecular model of ChCl-treated PAN. While positive and negative charges are shown, fibers were designed to have only one preferred charge. In the ball and stick model for ChCl, the color code is gray for carbon, blue for nitrogen, and red for oxygen.

**Positively Charged Electrospun Fibers.** PAN has been reported for efficient filtration of PM without offering much resistance to the air flow.<sup>15</sup> In our study, for cost-effectiveness, commercial-grade PAN was chosen to prepare the electrospun fiber mat. The morphology and physical dimensions of the electrospun fibers before and after treatment by ChCl are shown in Figure 2, respectively. The untreated fibers were



**Figure 2.** Scanning electron micrographs of electrospun PAN [(a) bare and (b) treated fibers] and PS [(c) bare and (d) treated fibers]. Scale bar corresponds to 5  $\mu$ m. Molecular models of chemically functionalized fibers: (e) ChCl-treated PAN and (f) SPS. In the ball and stick model, the color codes for carbon, oxygen, nitrogen, and sulfur are gray, red, blue, and yellow, respectively.

uniform without any beads, as shown in Figure 2a,b. The fiber diameter of the untreated fiber was  $\sim$ 300 nm, while after treatment with ChCl, it increased to  $\sim$ 450 nm, as shown in Figure S6a. This increase in fiber diameter might be due to the anchoring of choline moieties on the fiber. Upon treatment, webbing between the fibers was also observed, as shown in Figure 2b. The webbing could be due to interconnections formed between two neighboring fibers, caused by the

anchoring of the choline moiety and subsequent drying-related artifacts. Fourier transform infrared spectroscopy (FTIR) was performed on the untreated and ChCl-treated PAN to confirm the anchoring of choline groups on the fibers. The spectrum of PAN fibers shows several peaks, which are related to the existence of C-H, C≡N, C=O, and C-O bonds and associated groups, as shown in Figure S6b. The peak at 3430 cm<sup>-1</sup> corresponds to the N-H stretching frequency.<sup>45</sup> The peaks at 2938, 1453, 1357, and 1249 cm<sup>-1</sup> represent the aliphatic stretching C-H vibrations in CH, CH<sub>2</sub>, and CH<sub>3</sub>, while the peaks at 1700-1780 cm<sup>-1</sup> indicate the presence of C-O and C=O, possibly because of the presence of monomers of methacrylate found in commercial-grade PAN.<sup>53</sup> The peak at 1070 cm<sup>-1</sup> represents the C–N stretching present only in ChCl-treated PAN. The characteristic peak at 2250 cm<sup>-1</sup> represents the C $\equiv$ N bond, and the presence of this bond with a lower intensity in ChCl-PAN, compared to that in bare PAN, suggests the anchoring of the choline moiety on the fiber. Increased intensity of the C=O peak in ChCl-treated PAN and the presence of C-N stretching frequency also confirm the addition of the choline moiety onto PAN.5 Because of the overall positive charge of the choline moiety, upon anchoring with PAN, ChCl-PAN would attain this positive charge on the PAN fiber passively. Charge of PAN nanofibers before and after chemical treatment was measured by placing 20 mg of the fiber mat inside the Faraday cup, and the data are shown in Figure S7a. The untreated PAN fiber mat was added into the Faraday cup at the end of 10 s, and the charge of this mat was stabilized to  $\sim -8 \times 10^{-10}$  C. The ChCltreated PAN fiber mat was added to the Faraday cup at the end of 20 s, and the charge of this fiber was stabilized to  $\sim 1 \times 10^{-9}$ C. This confirms a positive charge on the ChCl-PAN fiber mat, relative to the untreated mat.

Negatively Charged Electrospun Fibers. Commercialgrade general-purpose PS was utilized for the preparation of negatively charged electrospun fibers. The morphology of the fiber before and after treatment with H<sub>2</sub>SO<sub>4</sub> is shown in Figure 2c,d. The untreated PS fibers displayed a narrow size distribution of around ~450 nm, but upon chemical treatment with  $H_2SO_4$ , the fiber diameter increased without any physical damage, as shown in Figure S4c, and the corresponding scanning electron microscopy (SEM) image is shown in Figure 2d. The fiber diameter after treatment increased to ~1000 nm, which could be due to the chemical treatment in the solution phase, causing a polymer chain relaxation. To confirm the presence of sulfonate groups anchored on the fibers, FTIR analysis was performed, as shown in Figure S6d. The presence of peaks at 3060, 2906, and 1460 cm<sup>-1</sup> corresponds to C-H aromatic, C-H alkyl, and C=C aromatic stretching modes, respectively.<sup>55</sup> The presence of a peak in the region of 1195-1168  $\text{cm}^{-1}$  is due to S=O stretching.<sup>44</sup> This peak, absent in untreated PS fibers, confirms the anchoring of sulfonate moieties onto PS. The overall charge of the sulfonate moiety is negative, and upon anchoring of this on PS fibers, they impart negative charge. Charge of PS nanofibers before and after chemical treatment was measured by placing 20 mg of the filter mat inside the Faraday cup, and the data are shown in Figure S7b. The untreated PS filter mat was placed inside the Faraday cup at the end of 10 s, and the charge of this mat was stabilized to  $\sim 2 \times 10^{-9}$  C. The SPS nanofiber mat was added to the Faraday cup at the end of 18 s, and the charge of this fiber mat was stabilized to  $\sim -4 \times 10^{-9}$  C. This confirms that the charge of the chemically treated PS fibers became negative.

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**Contact Angle Measurements.** To measure the contact angle of the fibers, PAN and PS were electrospun on glass slides for 30 min and subsequently treated with ChCl and sulfuric acid for imparting surface charges. The optical images obtained during the contact angle measurements are shown in Figure S8. The contact angles for untreated PAN and PS fibers were 102 and 98°, respectively, and upon chemical treatment, the contact angles subsequently reduced to 41 and 78°. This decrease in the contact angle could be due to the introduction of surface polarizability caused by chemical functionalization.

Assembly of the Filtration Mat. Ideally, the filtration mat should offer zero or negligible resistance to airflow. To obtain a near-ideal filter without compromising filtration efficiency, the electrospinning time for obtaining the fibers, as well as the number of NW mats utilized to make the filtration mat, was varied. Pressure drop across these filters was measured using AFET, and the values are shown in Figure S9a. A pressure gauge was used to measure the resistance offered to airflow. Fibers with 15, 30, 45, and 60 min of electrospinning duration combined with two or four NW mats were considered. The chemically treated fibers offered higher resistance to airflow compared to the untreated ones. The resistance to airflow increased with increase in electrospinning duration and with increasing number of NW mats. The pressure drop across the mats reached a maximum value of ~56 Pa chemically treated 4NW60 (four NW mats with the electrospun mat obtained after 60 min of electrospinning) mat. By varying the duration of electrospinning, the amount of fibers deposited on the NW mat was varied, which could affect the air resistance. The NW mat of  $13 \times 16$  cm weighed about 0.8 g, and the weight of the filter mat per fixed area for different electrospinning durations is shown in Figure S9c. We chose to use four NW mats and a spinning time of 30 min, as this combination offered minimal resistance without compromising on the filtration efficiency.

**Filtration of Fumed Silica Particles.** To understand how solid particles are captured, fumed silica was fluidized with a face velocity of 5 cm s<sup>-1</sup> using compressed air. These particles were loaded in a chamber, as shown in Figure S1. The particles were seen to be captured by the electrospun mat. SEM images of the bare PAN, PS, and chemically treated PAN and PS after exposure to the silica particles are shown in Figure 3. Figure 3a shows the SEM images of bare PAN fibers after exposure to



**Figure 3.** Scanning electron micrographs of fibers after exposure to fumed silica: (a) bare PAN, (b) ChCl-PAN, (c) bare PS, and (d) SPS. Scale bar corresponds to 50  $\mu$ m.

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**Figure 4.** Comparison of filtration efficiencies of treated and untreated fibers. (a) Photograph of the filtration setup used for trapping of soot particles (left) using fiber mats; hazy condition is created by the introduction of ~1413  $\mu$ g m<sup>-3</sup> of PM<sub>2.5</sub>. (Inset) Photograph of the PS mat; the circular region is due to the contact by soot for 60 min. (b) Comparison of the filtration efficiency in removing PM<sub><2.5</sub> and PM<sub>10</sub> of untreated PAN, PS, and combined (PAN + PS) fiber mats with the treated fibers. (c,d) Comparison of the time-dependent filtration efficiency of PM<sub>2.5</sub> and PM<sub>10</sub>, respectively, of the fibers.

silica particles. As the electrospun fiber mats are densely packed, they restrict the movement of the particles flowing through, thus effectively trapping the particles within. A similar phenomenon of trapping was observed for ChCl-PAN, PS, and SPS. Hang et al. reported during the filtration of soil dust that the particles come in contact with the fibers and subsequently get attached and grow as dendrites on the fibers.<sup>56</sup> This adhesion on the single fiber could be due to the presence of enhanced surface charges present because of chemical treatment. In the case of chemically modified PAN, webbing between fibers was observed, and this could enhance the filtration, as shown in Figure 3b, by offering more resistance for easy particle movement. In the case of SPS, upon chemical treatment, the fibers have a larger fiber diameter compared to untreated fibers, and this further restricts the movement of particles (as shown in Figure 3d). Because of this diameter change, webbing between fibers, and surface charges, we believe that the chemically treated fibers offer better filtration efficiency compared to the untreated ones.

**Filtration of Aqueous NaCl Aerosols.** During the generation of aerosols from aqueous NaCl, excess Na<sup>+</sup> and Cl<sup>-</sup> species are expected to be present. The input and output concentrations of these aerosols are measured by AFET, as shown in Figure S1. A comparison of the filtration efficiency of chemically treated and bare fibers is presented in the inset of Figure S10. For removing PM<sub>0.3</sub>, the filtration efficiency rose to ~93 ± 1.5% with an increment of ~3%. Similarly, for removing PM<sub>0.5</sub>, the efficiency rose to ~99.8 ± 0.6%, and it reached ~99.92 ± 0.2% for PM<sub>0.7</sub>, PM<sub>1</sub>, PM<sub>2</sub>, and PM<sub>3</sub>. The enhancement in capturing PM<sub>0.3</sub> by the chemically treated fibers is attributed to the presence of molecular charges on these fibers, as shown in Figure S10. This enhancement can also be due to the entanglement and webbing between individual fibers observed after chemical treatment. To

visualize the particles trapped by the fibers, NaCl concentration was increased to 60 wt % by weight, and it was aerosolized. The fibers were placed in AFET under continuous exposure of 10 min. Later, the fibers were dried and analyzed using SEM, as shown in Figure S10a. NaCl crystals trapped by chemically treated PS fibers are shown in the marked region of Figure S8a. The chemical composition of the crystal was determined by spot energy-dispersive spectroscopy (EDS). A semiquantitative view of the elemental composition in both atomic % and weight % is shown in the inset. Note that a slight Na excess is seen, and this is expected for sulfonated fibers as the negatively charged fibers attract positively charged (Na<sup>+</sup> excess) droplets. Typical bacteria range from 0.3 to 2  $\mu$ m in size;<sup>57</sup> because of this  $\sim$ 3% enhancement in removing PM<sub>0.3</sub>, we believe using our filters we can offer protection from bacterial aerosols. For filtering PM<sub>0.3</sub>, the QF was noted to be 0.11 for untreated fibers and 0.12 Pa<sup>-1</sup> for the chemically treated fibers, suggesting that the chemically treated fibers were slightly better compared to the untreated counterparts.

Filtration of Soot by Fibers. In the present work, in order to replicate a harsh and hazy environment, soot released from the burning of an incense stick was studied. The setup used for the filtration process of soot is depicted in Figure 4a, and the process is shown in Video S1. The mats which need to be tested were placed between the two bottles, and the smoke from the incense sticks was passed through them. The filtration efficiency was estimated by using a Perfect Prime AQ9600 particle counter. The input concentration of PM was ~1413 µg m<sup>-3</sup> of PM<sub>2.5</sub>. PS fibers (>95%) showed higher efficiency than PAN (>94%) in removing PM<sub>2.5</sub>, a result that contradicts other reports.<sup>15,58,59</sup> Because of 30 min of electrospinning duration, the fiber packing density increased, which could lead to these high filtration efficiencies. The highest filtration efficiency was observed in a system combining the chemically treated PAN

and PS fibers embedded between the PP membrane, and the efficiency was ~98.4% for PM<sub>2.5</sub> and ~99.9% for PM<sub>10</sub>. By combining the untreated PAN and PS fibers, the filtration efficiency was noted to be ~98% for PM<sub>2.5</sub> and ~99.3% for PM<sub>10</sub>. The filtration efficiency of PP was negligible at 13 and 18% in removing PM<sub>2.5</sub> and PM<sub>10</sub>, respectively, as shown in Figure 4b. We observed hazy condition in the second bottle as well while using the PP mats alone.

To systematically study the dependence of charge on the filtration efficiency, we have varied the input concentrations of ChCl and H<sub>2</sub>SO<sub>4</sub>. The concentration of ChCl was optimized to 216 mM. Upon doubling the concentration, there was a loss in the structural integrity, making the fiber mat brittle. The scanning electron micrograph of the 432 mM ChCl-treated PAN fiber is shown in Figure S11b. The porosity was greatly reduced because of the increased webbing between the neighboring PAN fibers. The pores are highlighted with yellow arrows and are represented in white circles. The charges of the PAN fibers with three different concentrations of ChCl are shown in Figure S11a. With increasing concentration of ChCl, we observed higher positive charge, which increased the filtration efficiency of ChCl-PAN, as shown in Figure S11c. However, this reduction in porosity increases the pressure drop, making it difficult to breathe, and because the mat was brittle, this could lead to easy cracking, eventually decreasing the overall filtration efficiency. To impart negative charges on electrospun PS fibers, these fibers were treated with H<sub>2</sub>SO<sub>4</sub>. The concentration of H<sub>2</sub>SO<sub>4</sub> was optimized to 3 M, and charges of these fibers at different concentrations are shown in Figure S12a. By doubling the concentration of  $H_2SO_4$ , the amplitude of charge increased marginally. The filtration efficiency shown in Figure S12b showed an increase with doubling concentration of H<sub>2</sub>SO<sub>4</sub>. However, the increase was only  $\sim 1\%$ .

To understand the performance of the mat under harsh conditions for longer durations, a time-dependent filtration test was performed by leaving the filters in the harsh condition for 1 and 24 h. The output concentration of soot particles was studied periodically every 15 min to investigate the saturation point. The filtration efficiencies exhibited by untreated and treated fibers in removing PM2.5 and PM10 are shown in Figure 4c,d. We observed a decrease in the filtration efficiency by the untreated fibers as the time progressed. This decrease was from 95.3 to 92.9% for PAN and from 98.5 to 91.2% by PS in removing PM<sub>25</sub>. For chemically treated PAN and PS fibers, this decrease was minimal. However, by sandwiching the treated PAN and PS fibers between two PP NW mats, the consistent filtration efficiency of ~99.9% in removing  $PM_{2.5}$  for the entire duration of 1 h was observed. Similar trends were observed during the removal of PM<sub>10</sub>. The filtration efficiency saw a decline as the time progressed in the case of untreated fibers. On the other hand, the combined filter mat maintained the efficiency at ~99.9%.

The SEM images of soot trapped by the bare and chemically treated PAN and PS after exposure to soot for 60 and 86,400 s are shown in Figure 5. The SEM images of bare PAN after exposure to soot for 60 and 86,400 s are shown in Figure 5a(i,ii), respectively. The soot particles were seen to be trapped by the fibers everywhere on the mat. During longer exposure to soot, webbing was observed between adjacent fibers and attributed to soot aggregation, as shown in Figure 5a(ii). Similar phenomena were observed for the ChCl-PAN, bare PS, and SPS mats. The excessive morphological change observed



**Figure 5.** Scanning electron micrographs of fibers after soot deposition: (a) bare PAN fibers, (b) ChCl-PAN, (c) bare PS, and (d) SPS fibers. Scale bar corresponds to 50  $\mu$ m. Images (i,ii) in each correspond to 60 and 86,400 s of exposure.

in ChCl-PAN and SPS during extended soot deposition is possibly a major reason for the enhancement in filtration efficiency.

Filtration Efficiency of the Mat. After studying the performance of individual fibers, we studied the performance of mats prepared using these fibers. A typical mat consists of either treated or untreated PAN and PS fibers sandwiched between four NW PP mats. The average filtration efficiency of six samples of untreated and treated mats under long exposure to soot is shown in Figure 6a,b. In the case of the untreated fiber mat, the filtration efficiencies at the end of 1 h were  $\sim$ 98.0  $\pm$  0.5 and 99.3  $\pm$  0.35% for removing PM<sub>2.5</sub> and PM<sub>10</sub>, respectively, as shown in Figure 6a. This efficiency further increased to ~99.6  $\pm$  0.25% (PM<sub>2.5</sub>) and ~99.8  $\pm$  0.2%  $(PM_{10})$ , respectively, after 10 h of exposure. Finally, at the end of 24 h, this efficiency reached a maximum of  ${\sim}99.92\pm0.07\%$  $(PM_{2.5})$  and ~99.92 ± 0.07%  $(PM_{10})$ , respectively. This enhancement in filtration could be due to the morphological change of fibers caused by extended exposure to soot. The filtration efficiencies for the treated fiber mat are shown in Figure 6b, which at the end of 1 h of exposure were  $\sim$ 99.07 ± 0.07% (PM\_{2.5}) and ~99.9  $\pm$  0.07% (PM\_{10}), respectively. It reached ~99.92  $\pm$  0.07% for both PM<sub>2.5</sub> and PM<sub>10</sub> at the end of 10 h. The capture efficiencies at the end of 24 h were



**Figure 6.** (a,b) Long-term filtration efficiencies of  $PM_{2.5}$  and  $PM_{10}$  by the untreated fiber mat and chemically treated fiber mat of different masses, respectively. (c) Schematic of the filtration setup, and filters were placed between two glass bottles wherein the soot particles were introduced in the left bottle. (d) Comparison of the PM removal efficiency between untreated and treated filter mats. VOC uptake by the fiber mat after 1 h of exposure to (e) THF, (f) aniline, (g) toluene, and (h) chloroform.

~99.92  $\pm$  0.07 and ~99.92  $\pm$  0.07% for PM<sub>2.5</sub> and PM<sub>10</sub>, respectively. The enhanced capture efficiency is due to morphological changes inherent to the treated fibers. However, the fibers were completely enveloped by soot at the end of 24 h in the case of treated fibers. Under extreme harsh and hazy conditions, we believe that the chemically treated fiber mat is preferable over the untreated mat.

While testing the long-term filtration efficiency, soot particles did settle down, forming a yellow colored precipitate. To circumvent the issue of the settling of PM, the chamber was saturated with soot, the particles were fluidized with a face velocity of 0.3 mL min<sup>-1</sup>, and the filtration efficiency was noted. The schematic of this modified setup is shown in Figure 6c. The filtration efficiency under the forced movement of soot is shown in Figure 6d.

The pressure drop across the filter mat before and after filtration is shown in Figure S9b. To measure this pressure

drop, a digital manometer was placed across the filter mat in the soot filtration setup. Here, air flow was created by using the IPM-191 dust collector, which has variable flow rates of 5 and 8 L min<sup>-1</sup>. The fresh untreated filter mat had pressure drops of 82 and 608 Pa at the flow rates of 5 and 8 L min<sup>-1</sup>, respectively. This pressure drop increased when the untreated filter mat was exposed to soot for 24 and rose to 100 and 690 Pa, respectively. A similar trend was observed in the case of the treated filter mat, where the initial pressure drops were 91 and 651 Pa, which then increased to 131 and 700 Pa, respectively. This increase in pressure drop is predominantly due to the blockage of the pores caused by aggregated soot particles after filtration. The pressure drop across both the untreated and treated filters before exposure to soot is comparable to the pressure drop of the commercial-grade N95 filter mask.<sup>60</sup> The QF, also known as the figure of merit, was used to evaluate the performance of the filter mat. For the flow rates of 0.3, 5 and 8

L min<sup>-1</sup>, the untreated fibers had QFs of 0.07, 0.04, and 0.006  $Pa^{-1}$ , respectively. In the case of the treated filter mat, the QFs are 0.08, 0.05, and 0.007  $Pa^{-1}$  for the flow rates of 0.3, 5, and 8 L min<sup>-1</sup>, respectively. The QF values indicated that the treated fiber mats performed better under different flow rates compared to the untreated fibers. A comparison of filtration efficiency and pressure drop of the untreated and chemically treated filter mat is shown in Table 1.

# Table 1. Comparison of Different Properties of Untreated and Treated Fibers

property	untreated filter mat	treated filter mat
pressure drop (Pa) @ 16 L min <sup>-1</sup> flow rate <sup><math>a</math></sup>	24	28
Pressure drop (Pa) @ 5 L min <sup>-1</sup> flow rate		
before soot deposition	82	690
after soot deposition	100	608
pressure drop (Pa) @ 8 L min <sup>-1</sup> flow rate		
before soot deposition	91	651
after soot deposition	131	700
filtration efficiency (PM <sub>0.3</sub> ) (%)	$\sim 89 \pm 1.3$	~93 ± 1.3
forced soot filtration at a flow rate of $0.3 \text{ mL min}^{-1}$		
PM <sub>2.5</sub>	97.2	99
PM <sub>10</sub>	98.4	99.5
natural soot filtration		
PM <sub>2.5</sub>	98	99.8
PM <sub>10</sub>	99.3	99.9
electrospinning time of 30 min		
mass of PAN (g)	0.15	0.21
mass of PS (g)	0.25	0.32
QF (Pa <sup>-1</sup> ) for removing PM <sub>0.3</sub> having a face velocity of 5 cm $s^{-1}$	0.11	0.12
<sup><i>a</i></sup> Mat area is 10 cm <sup>2</sup> here, and for others, it	t is 4 $\mathrm{cm}^2$ .	

VOC Uptake by Electrospun Fibers. Recent studies have concluded that electrospun polymer fibers and their composites are capable of capturing VOCs. Similar studies were performed to determine the maximum VOC uptake by the fibers. Electrospun fiber mats of different masses-2, 10, and 20 mg were taken, and their uptake capacities for model VOCs such as THF, toluene, chloroform, and aniline were studied for a duration of 1 h. These fibers were later immersed in ACN to leach out adsorbed VOCs. This solution was analyzed using HPLC to determine the analyte concentrations, and the data are shown in Figure 6e-h. From Figure 6e, the maximum uptake of THF was observed for 20 mg of untreated PAN and PS fibers, and this was reduced for the chemically treated ones. A similar trend was also observed for 10 mg mass. However, SPS captured ~3 ppm more than ChCl-PAN, whereas PAN captured ~2 ppm more than PS. We observed that even 2 mg of the electrospun fiber mat captured THF, and the maximum amount captured was  $\sim 1$  ppm. The uptake of aniline by the electrospun fibers is shown in Figure 6f, where the maximum capture was observed by 20 mg of PS fibers reaching ~55 ppm and the SPS fibers captured ~40 ppm of aniline. For aniline, ChCl-PAN showed a higher capture than PAN fibers. Similar trends were observed for 10 and 2 mg of the material. PS fibers of 2, 10, and 20 mg captured the maximum amount of aniline. Capture of toluene by the electrospun fibers is shown in Figure 6g, and the maximum capture was observed for the chemically treated fibers compared to the bare fibers, SPS > PS, and ChCl-PAN >

PAN. We observed a similar trend for both 2 and 10 mg, and the smallest amount of 0.8 ppm was captured by 2 mg of PAN electrospun fibers. Capture of chloroform by the electrospun fibers is shown in Figure 6h, in which PAN fibers of 20 mg captured the maximum amount compared to PS fibers; however, upon chemical treatment, ChClPAN captured lesser. PS fibers also captured lesser amount when compared to their chemically treated counterparts. Similar trends were observed for both 2 and 10 mg of fibers, and the smallest amount of ~1.5 ppm was captured by 2 mg of the fibers. From Figure 6e-h, electrospun fiber mats both treated and untreated are capable of capturing model VOCs, and because of the chemical functionalization, the treated fibers had lower uptake capture when compared to the untreated ones.

Antibacterial Activity. Digital photographs of the agar plate containing E. coli, B. subtilis, and E. faecalis with the fiber mats are shown in Figure S13. An agar plate containing E. coli with the filter mats is shown in Figure S13a, and a visible zone of inhibition along the filter mat was observed for PAN, PP, ChCl-PAN, and SPS. E. subtilis containing an agar plate along with the filter mat is shown in Figure S13b, and similar to E. coli, a visible zone of inhibition was observed for PP, PAN, and ChCl-PAN. Finally, the agar plate containing E. faecalis along with the filter mats is shown in Figure S13c, and a small zone of inhibition was observable in the case of PAN, ChCl-PAN, and PP mats. It is evident from these zones that PAN, ChCl-PAN, and PP show slight susceptibility for the antibacterial activity; however, the zone of inhibitions is not signification when compared with that of antibiotics. PS fibers did not show any antibacterial activity toward any of the bacteria used. We conclude that these fibers are repulsive to the tested bacteria and thus suitable to be used inside a nasal plug for extended periods of time.

In order to determine the practical applicability of the filtration mat in real-life conditions, a silicone-based nasal plug was procured, and the mat was placed inside this nasal plug. Ten volunteers were asked to use the nasal plug and 90% of them did not experience any discomfort while breathing using the nasal plug. The comfort of breathing was similar to that of a commercial-grade N95 mask.

#### CONCLUSIONS

Chemically functionalized PAN and PS fibers offer better filtration efficiency for removing PM compared to the untreated counterparts. They were also capable of adsorbing VOCs. The enhancement in filtration efficiency was suggested to be primarily due to the morphological change observed after chemical treatment and also due to the presence of surface charges. A filtration mat was assembled using four NW PP mats and employing an optimized electrospinning time of 30 min to obtain PAN and PS fibers. The fibers were functionalized with +ve and -ve charges by chemical treatment after electrospinning. Under hazardous environments, these chemically functionalized mats maintained a filtration efficiency of ~99.92  $\pm$  0.07% in removing PM<sub>2.5</sub> and PM<sub>10</sub>. The mats offer minimum resistance to air flow, with the maximum pressure drop across the fibers being <60 Pa. Pressure drop across the untreated and treated filter mats was measured at 5 and 8 L min<sup>-1</sup> air flow. The untreated fibers offered resistances of 82 and 608 Pa, respectively, before exposure to soot. After exposure to soot for 24 h, this resistance increased to 100 and 690 Pa, respectively. The chemically treated filter mats before exposure to soot offered

resistances of 91 and 651 Pa, respectively, which increased to 131 and 700 Pa after exposure to soot for 24 h. The QF indicates that at these flow rates, the chemically treated filter mat offered better filtration efficiency with a lower pressure drop. The untreated and treated fibers were tested for their antibacterial property, and using the zone of inhibition method, *E. coli, B. subtilis,* and *E. faecalis* were tested. PP, PAN, and ChCl-PAN presented a visible zone near the mat, suggesting the presence of antibacterial property in these fibers. Because of this antibacterial property, the filters can be used for extended duration. We believe such mats can be used in nasal plugs for personal protection.

#### ASSOCIATED CONTENT

#### **Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acssuschemeng.9b06853.

Schematic of AFET; soot filtration setup; particle size and zeta potential; charge and dust distribution of dust; XRD of dust; FTIR and fiber diameter distribution; filtration efficiency using NaCl aerosol; contact angle measurement; pressure drop measurement; antibacterial testing; and charge distribution on fibers (PDF)

PAN (TXT)

ChCl-PAN (TXT)

PP (TXT)

SPS (TXT)

Soot filtration (MP4)

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#### Notes

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