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Electrospun membranes filtering 100 nm particles from air flow by means of the van der Waals and Coulomb forces

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ABSTRACT

Nonwoven fibrous filter membranes are widely used in filtration because of their low cost. They are less effective in intercepting airborne particles of the order of 100 nm, which is of the SARS-CoV-2 (COVID-19) virus’s size. Many diseases, including COVID-19, predominantly spread by droplets released by breathing, coughing, sneezing, or medical procedures. It was shown that the smallest droplets can evaporate in air before settling, thus, making viruses airborne and easily penetrating even the best masks and filters. As a result, air-filtering membranes, which are capable of effective interception of ~100 nm nanoparticles are highly desirable. A traditional way to improve filtration efficiency by overlapping several layers of nonwoven fabrics increases the required pressure drop, and thus, should be avoided as much as possible. Here, we propose and demonstrate an innovative approach to enhance performance of filtration membranes based on (i) a dramatic reduction in the fiber size, and (ii) metal coating of the fibers. The first component of this approach allows one to incorporate a novel physical mechanism of filtration, the short-range van der Waals forces, whereas the second one adds the long-range electric Coulomb forces if the oncoming nanoparticles are pre-charged and the metal-plated membrane grounded. In the present work, the ~100 nm aluminum nanoparticles are filtered as a model of commensurate airborne single COVID-19 viruses, and Platinum is used as the sputter-coated material for the fiber coating. The resulting filtration efficiency enhanced by the electric Coulomb forces alone is increased by the factor of 1.77, while the filtration efficiency additionally facilitated by the van der Waals forces increased by the factor of 2.44. In comparison to the filter membranes with ~500 nm fibers without the electric forces involved, the van-der-Waals-electric filter membrane with fibers ~90 nm is 2.24 \(\times\) 1.77 = 3.96 times more effective. The quality factor of a membrane which combines the van der Waals and Coulomb forces is 10.6 psi \(^{1}\), which is almost three times that of a comparable membrane without the electric Coulomb force (with only van der Waals forces being used).

1. Introduction

Transmission of detrimental nanoparticles (NPs) in air has always been a critical problem for human health. NPs are defined as small particles in the 1–100 nm range. They could possess medical benefits, health hazards, and toxicity aspects \([1]\). On one hand, nanomedicines developed based on unique properties of NPs and nanostructures are produced for drug delivery in case of such lethal diseases, as cancer \([2]\). On the other hand, some toxic nanoparticles also exist, many of them are metal-based and could easily penetrate into human body causing severe health problems on skin, via ingestion and inhalation, and so on \([3]\). The recent worldwide pandemic caused by the SARS-CoV-2 (COVID-19) virus presents another example of an airborne toxic nano-particle. According to the recent data, spreading of COVID-19 is mainly through breathing, coughing or sneezing of virus-containing droplets of less than 20 \(\mu\)m in size, or due to a similar aerosolization caused by medical procedures, e.g., in dentistry \([4–7]\). For aerosols, whose size is larger than 5 \(\mu\)m, the surgery and N95 masks could effectively reduce the risk of virus transmission \([8,9]\). It should be emphasized that aerosols could be virus-laden droplets, which do not necessarily immediately come in contact with a filter, but first evaporate in flight. Those of them which evaporate before settling (\(<20 \mu\)m in stagnant air, or even larger,

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Commercial filters are mostly formed from nonwoven fabrics, which provide good filtration efficiency and low cost. In addition, membranes incorporating nanofibers still possess sufficient permeability, which makes filtration energy-efficient, and filter media low-weight. Such nonwovens can be coupled with other functional materials to enhance their filtration efficiency [13–15]. Fabric-based filter membranes can be formed with such materials as cellulose, thermoplastics, fiberglass, and so on [16–19]. The nanofiber-containing nonwoven fabrics can be manufactured using different processes, such as electrospinning, meltblowing, spunbonding, solution blowing, supersonic solution blowing, etc. [20–29]. Electrospinning results in nonwoven membranes, which possess relatively small pores and large specific surface area, with both features significantly enhancing the membrane filtration efficiency [30, 31]. In electrospinning, a polymer solution is issued as a jet from a needle, which also serves as an electrode, whereas a metal collector located at some distance serves as a counter-electrode. The electric field between the electrodes, also acts on the polymer solution jet (a leaky dielectric, which acquired a net charge). As a result, such a polymer jet is stretched, undergoes significant electrically-driven bending instability (i.e., a significant additional stretching), solvent evaporates in flight, polymer precipitates, which results in micro/nanotextured nonwoven membranes deposited onto the counter-electrode collector [22,25]. Electrospun webs are widely used in many filtration fields. For example, as absorbing versatile organic compounds in air [32], protective clothing from nanoparticles [33], or antibacterial filter media [25,34].

Innovations in the field of fibrous filtration membranes mostly stem from two aspects. One is related to changes in the physical characteristics of fibers, such as the fiber material, size, and so on. For example, the effect of nonwoven fiber characteristics on filter efficiency was studied in [35]. It was found that the filtration efficiency would increase at smaller fiber size and rougher fiber surface. Blends of bi-modal-sized fibers (in the 10 μm to 20 μm range) would also improve filtration efficiency when the filter medium contains much more fine fibers than coarse fibers and the particle sizes are over 180 nm. A limited effect of SVF (Solid Volume Fraction) on the filtration efficiency was also demonstrated [35–37].

The physical origin of the van der Waals forces is in different types of the dipole-dipole interactions between electroneutral molecules, which are typically lumped in the Hamaker constant [38–40]. The van der Waals force acting between a particle and a straight filament depends on their radii, the Hamaker constant and the distance between their centers and is given by Eq. (10) in Ref. [41]. The van der Waals force is relatively short-range ~100 nm, accordingly, it becomes a significant factor for fibers which do not displace the oncoming flow for more than ~100 nm, while the displacement is of the order of the fiber cross-sectional size. The smallest fiber sizes in the 20 nm–50 nm range could be achieved by means of the supersonic solution blowing [26]. Accordingly, these nanofibers introduce an additional physical mechanism of nanoparticle interception in the short range ~100 nm from the collector (a fiber), specifically, the van der Waals forces [41]. Another attractive aspect is associated with changing the fiber surface properties by introducing different chemical or metal coatings (serving as electrodes), the latter to allow for an additional electric Coulomb force being employed in the filtration process. The electric force is a relatively long-range force and, according to Coulomb’s law, its magnitude is equal to the product of a particle charge and the magnitude of the local strength of the electric field [42]. For instance, meltblown polypropylene nonwovens were coated with N-halamine polyelectrolytes in order to achieve antimicrobial properties [43]. Metal-coated micro- and nanofiber fibrous membranes were formed by metal-plating of electrospun polyacrylonitrile (PAN) nanofibers in Ref. [44]. Such metal-plated filter

Fig. 1. SEM images of aluminum (Al) nanoparticles of the size of ~100 nm after 30 min sonication.
membranes serving as an electrode with an applied voltage were found to be very efficient for interception of particulates of different sizes (e.g., <2 μm), charcoal powder of the size of 500 μm, and for smoke filtration process [45,46]. Recently, such filters were even used to form novel face masks [47]. As for the virus filtration, filters are mostly developed having in mind the following four aspects: the mechanical, geometrical, electrical and chemical modifications of the membrane features, or the combination of the above features. For instance, performance of an electrochemical carbon-nanotube filter for virus removal from drinking water was explored in Ref. [48]. Also, a nanocellulose filter paper for influenza virus removal based on controlling the nonwoven fiber size was proposed in Ref. [49].

An effective filtration of airborne nanoparticles of the COVID-19 virus size of ~100 nm is still a challenging problem in spite of multiple researches conducted with some promising results. Such small particles call for the novel filtration membranes with ultra-fine submicron fibers employing the van der Waals and electric Coulomb forces. The present work aims at formation of such ultra-fine membranes and a detailed investigation of their filtration efficiency using ~100 nm aluminum (Al) nanoparticles as a model particulate material. The model Al nanoparticles first of all mimic the virus size and shape, with COVID-19 virus being roughly spherical with the gyration radius up to ~125 nm, which is close to the parameters of the Al nanoparticles used. Therefore, the Al nanoparticles are used here as not-so-dangerous surrogates of viruses, which is a common practice in many fields. The commensurate size of the surrogate Al nanoparticles to that of COVID-19 viruses guarantees that both are subjected to very similar electric and van der Waals forces, which are determined by their sizes and the corresponding physical aspects, while still being totally different in the degree of their danger associated mostly with chemical and biochemical aspects. It should be emphasized that the surrogate Al nanoparticles in the present work are initially suspended in water droplets, while COVID-19 viruses are initially suspended in water droplets, particles in the present work are initially suspended in water droplets, and a detailed investigation of their filtration efficiency using ~100 nm Al nanoparticles was performed in Ref. [49].

A suspension would be ultrasonically vibrated in a bath sonicator (Cole-Parmer) for 30 min every time before conducting filtration experiments. An effective filtration of airborne nanoparticles of the COVID-19 virus size of ~100 nm is still a challenging problem in spite of multiple researches conducted with some promising results. Such small particles call for the novel filtration membranes with ultra-fine submicron fibers employing the van der Waals and electric Coulomb forces. The present work aims at formation of such ultra-fine membranes and a detailed investigation of their filtration efficiency using ~100 nm aluminum (Al) nanoparticles as a model particulate material. The model Al nanoparticles first of all mimic the virus size and shape, with COVID-19 virus being roughly spherical with the gyration radius up to ~125 nm, which is close to the parameters of the Al nanoparticles used. Therefore, the Al nanoparticles are used here as not-so-dangerous surrogates of viruses, which is a common practice in many fields. The commensurate size of the surrogate Al nanoparticles to that of COVID-19 viruses guarantees that both are subjected to very similar electric and van der Waals forces, which are determined by their sizes and the corresponding physical aspects, while still being totally different in the degree of their danger associated mostly with chemical and biochemical aspects. It should be emphasized that the surrogate Al nanoparticles in the present work are initially suspended in water droplets, while COVID-19 viruses are initially suspended, for example, in saliva, which is a dilute aqueous solution of proteins, essentially very close to water in its properties [50]. Commensurate submicron droplets evaporate in flight at the same rate, which results in airborne surrogate Al nanoparticles or in reality in airborne COVID-19 viruses [4].

2. Experimental method

2.1. Materials

Polyacrylonitrile (PAN, M_w = 150,000 Da) and polycaprolactam (Nylon 6, molecular weight of repeated unit of 104.83 Da) were used in the present work to form fibers. PAN solutions were prepared at 6 wt % and 10 wt % in dimethylformamide (DMF) used as a solvent. Nylon 6 solution was prepared at 17 wt % in 88% formic acid used as a solvent. Nitric acid diluted to 10 wt % was used for the end gas cleaning from residual aluminum particles (if any). All the above-mentioned chemicals and 10 wt % in dimethylformamide (DMF) used as a solvent. Nylon 6 (Nylon 6, molecular weight of repeated unit of 104.83 Da) were used in the present work to form fibers. PAN solutions were prepared at 6 wt % while COVID-19 viruses are initially suspended, for example, in saliva, which is a dilute aqueous solution of proteins, essentially very close to water in its properties [50]. Commensurate submicron droplets evaporate in flight at the same rate, which results in airborne surrogate Al nanoparticles or in reality in airborne COVID-19 viruses [4].

2.2. Electrospinning

A single-nozzle setup similar to that of [51] was used for polymer electrospinning, as sketched in Fig. 2. Nanofibers were electrospun onto a copper mesh comprised of 0.36 mm-diameter wires, with the 44% open area. The copper mesh was fixed on a wheel, which could be swirled by a motor to facilitate uniformity of the deposited membrane. A DC high-voltage power source series EH was obtained from Glassman. Polymer solution was supplied by the NEW ERA NE-300 syringe pump. Positive electrode of the power supply was connected to the syringe needle (22G or 27G), while the motor and the attached copper mesh were grounded. The process parameters are listed in Table 1.

2.3. Metal-plating of fibers

The effect on filtration of the electric field associated with metal-plated fibers is one of the key factors studied in the present work. Sputter coating and electroplating were the two methods utilized for metal-plating of fibers. Fig. 3a depicts how fibrous membranes were sputter-coated with 10 nm platinum on both sides by a sputter coater (Technics Hummer Model V). Sputter coating might be the only metal-plating step, or the first step prior to electroplating. In the latter case sputter coating facilitates the electrical conductivity of the fibrous membranes before they could be used as an electrode in the
electroplating bath consisting of 25 g of sulfuric acid, 80 g of copper sulfate, 2.5 g of hydrochloric acid, 50 g of formaldehyde and 0.5 L of deionized (DI) water, cf. Fig. 3b. For electroplating, the sputter-coated fibrous membrane (a cathode) and a copper plate (an anode) were fully submerged in electrolyte facing each other, and connected to a DC power source provided by the electroplating station EPS-30A obtained from Technical Supermarket, with the applied voltage of 3 V. After electroplating, the membrane was immediately submerged into fresh DI water to rinse the residual electrolyte. Next, the membrane was placed in vacuum chamber for 12 h. After that, it was ready for the filtration
experiments. The images of fibrous membranes before surface treatment, after sputter coating, and after electroplating are presented in Fig. 4a, b and c, respectively.

2.4. Filtration experiments

2.4.1. Experimental setup

The filtration experimental setup (cf. Fig. 5) was designed and built to test and compare the filtration efficiency of different filter membranes prepared in the present work. A suspension of Al nanoparticles in DI water described in section 2.1 was used as a working fluid to simulate droplets carrying COVID-19 viruses. The suspension was aerosolized using ultrasonic humidifier, and the resulting mist was carried away by compressed air flow through the inlet channel of the ionizer. The filter membrane was installed in the tube, and after the filter membrane and the subsequent commercial filter the air flow was issued into a vessel filled with the 10 wt % nitric acid solution in DI water (cf. Fig. 5).

The high-frequency DC Ionizer ZappAURA used to charge the oncoming droplets/nanoparticles before the filter membrane was purchased from Static Clean and operated with the output voltage of 3 kV. The tested filter membrane was installed between the second and third tube sections (Fig. 5). At the end of the third tube section, a high efficiency particulate air (HEPA) vacuum bag purchased from Kenmore was installed to filter particles not captured by the filter membrane. The air flow behind the commercial filter, in principle, could still contain nanoparticles. To eliminate them from the exhaust, the flow was blown into the wash bottle filled with diluted nitric acid (Fig. 5). There, the following reaction between the aluminum nanoparticles and nitric acid would be taking place: $\text{Al} + 4\text{HNO}_3 \rightarrow \text{Al(NO}_3)_2 + \text{NO}_3^− + 2\text{H}_2\text{O}$ (note that another reaction is possible to eliminate the exhaust Al nanoparticles: $\text{Al} + 2\text{NaOH} + 6\text{H}_2\text{O} \rightarrow 2\text{Na}_3\text{Al(OH)}_6 + 3\text{H}_2\text{O}$). These guaranteed that the exhaust contamination by Al nanoparticles would be minimal (if any).

2.4.2. Experimental process

Compressed air at 15 psi was used as a carrier flux in all the filtration experiments. The filtration process lasted from the moment the mist generator had been turned on, and until it had been turned off. Aluminum nanoparticles were charged in the first section of the tube (cf. Fig. 5), and carried by the air flux though the grounded filter membrane, and (if not intercepted) further on through the commercial filter and into the nitric acid vessel. Note, that if the original droplets would be charged, after their evaporation the charge stayed on the resulting airborne nanoparticles. After shutting down the mist generator, compressed air was still pumped for 20 s in order to assure that the remaining airborne droplets/nanoparticles are purged from the system. When ionized air was needed for charging nanoparticles, the ionizer was turned on 20 s before the mist had been produced, so that the system was full of ionized air in advance.

2.5. Measurement of percentage of intercepted nanoparticles

Filter performance is often characterized by the Quality Factor,

$$QF = \frac{-\ln(1 - E)}{\Delta P}$$  

where $E$ is the filter efficiency, and $\Delta P$ is the pressure drop. Because the electrospun membranes already possessed a relatively low pressure drop, improving the efficiency would open a practical way of increasing QF in the present case [52]. Note that the units of QF are the inverse of the units of pressure. The efficiency is determined by the percentage of particles intercepted by the filter medium, which can be quantified as [53].

Fig. 6. SEM images of the (a) original nonwoven membrane with Al nanoparticles or their clusters intercepted; (b) binary image with the background originating from that of Fig. 6a; (c) binary image with only white particles and their clusters formed from the one in Fig. 6b. All the scale bars are 5 μm.
\[ E = 1 - \frac{1}{\beta} \]  

(3)

where

\[ \beta = \frac{N_u}{N_d} \]  

(4)

Here \( N_u \) is the number of particles per unit volume upstream the filter, while \( N_d \) is the number of particles per unit volume downstream the filter. Accordingly, the number of particles intercepted by the filter is expressed as \( N_i = N_u - N_d \), which transforms Eqs. (3) and (4) to the following form

\[ E = \frac{N_i}{N_u} \]  

(5)

In the present work, the air flux was constant, and thus, \( N_u \) constant, whereas \( N_i \) was determined by the membrane type. It will be explored as discussed below. The membranes used here were extremely thin, with only a few layers. They were exposed for a very short time for a clear visualization of the intercepted particles. Essentially, these membranes could be considered as 2D films, and a visible number of intercepted particles used to estimate \( N_i \). In addition, the total area of every image used for such an analysis was exactly the same, so the visible intercepted particles are representative of the value of \( N_i \) for the entire membrane.

To calculate the intercepted particle percentage using Scanning Electron Microscopy (SEM) images of the filter membrane taken after the filtration experiments, an image processing method was developed as follows. An original SEM image in Fig. 6 reveals a filter membrane with Al nanoparticles (~100 nm) and their clusters, which originated from the evaporation of suspension mist droplets in flight and were intercepted by the membrane. By applying a light threshold value, which is between 0 and 1, Fig. 6a can be converted into a binary-code image by replacing pixels with luminance greater than the threshold value with 1 (white) and all other pixels - with 0 (black), as shown in Fig. 6b [23,24]. As a result, a clear visualization of the particle-laden membrane and the background can be achieved. In addition, some small and blurry fibers can be removed from the image. To obtain images with only particles being seen, the fibers should be removed from the images. The fibers are seen as lines in the images, whereas the particles and their clusters are the blob-like objects (Fig. 6b). Accordingly, using a chosen threshold of the lateral size, the blob-like objects in the images were separated and the particle-alone image shown in Fig. 6c was obtained. In that image the particles or their clusters are white blobs seen on the black background. Therefore, the percentage of the membrane area covered by the particles can be calculated. This is done having in mind that the total area of every image was set to be exactly.

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Fig. 7. SEM images of PAN nanofibers electrospun from DMF solutions with PAN concentration of (a) 8 wt % and (b) 10 wt %. The corresponding average fiber sizes are ~209 nm and ~488 nm, respectively. The scale bars are 1 \( \mu \)m.

Fig. 8. SEM images of the sandwich filter membrane with bi-modal nanofiber sizes after air filtration with airborne Al nanoparticles. The average size of the thicker fibers is ~488 nm, while that of the thinner ones is ~114 nm. The scale bars are: (a) 10 \( \mu \)m and (b) 5 \( \mu \)m.
3. Results and discussion

3.1. Effect of the fiber cross-sectional size on nanoparticle interception

The dependence of the efficiency of a filter membrane on the cross-sectional fiber size was investigated using nanoparticles ~100 nm. The filter membrane was formed from fibers of two sizes. In order to obtain fibers with clearly discernible size difference, several concentrations of PAN in DMF were used in electrospinning. The average fiber sizes obtained with concentration of 8 wt % and 10 wt % were ~209 nm and ~488 nm, respectively, as measured using SEM images (cf. Fig. 7) and ImageJ processing software. It was found that the cross-sectional fiber size decreased with the solution concentration, in agreement with the results in [54]. Therefore, to form a filter membrane comprised of fibers of two clearly discernible sizes, electrospinning of PAN solutions in DMF with concentrations of 6 wt % and 10 wt % were employed. Both solutions were mixed by a magnetic stirrer for 24 h at room temperature. The first layer of the sandwich film was formed by electrospinning the 10 wt % PAN solution onto a rotating copper mesh, which provided mechanical support and served as an efficient collector. Then, the second layer was deposited by electrospinning fibers from the 6 wt % PAN solution. Filtration tests were conducted using the sandwich filter membrane using the experimental setup of Fig. 5. The supply rate of the particles (which are suspended in airborne water droplets) from the humidifier was 0.37 mg of particles per minute; the latter was estimated using the rate of suspension consumption and the particle concentration in it. The average fiber size was ~114 nm for the fibers formed from the 6 wt % PAN solution, and ~488 nm for the fibers formed from the 10 wt % solution. The scale bars are 10 μm.
PAN solution. The SEM images of the sandwich membrane after the filtration experiment shown in Fig. 8 reveal that it was able to intercept multiple particles. However, most of the nanoparticles and their clusters were collected by the thinner fibers. This conclusion is corroborated by the microscopic images of the same sandwich filter membrane taken by the optical microscope Olympus Q using Color 3 microscope camera. Note that the panels in Fig. 9a and b depict the same location at the filter membrane but illustrate the layer of the thicker, and the thinner fibers, respectively. The latter clearly intercepted much more particles.

In addition, the Brunauer-Emmett-Teller (BET) surface area analysis for both membranes was conducted using the Autosorb IQ-MP Vilton from Quantachrome. The results revealed the surface area values of 287 m$^2$/g for the membrane formed from the 6 wt % PAN solution and 104 m$^2$/g for the one formed from the 10 wt % PAN solution. This reveals that the surface area of the membrane comprised of the thinner fibers was almost three times that of the membrane comprised of the thicker fibers. Accordingly, not only the van der Waals forces would participate in the nanoparticle interception on the membrane comprised of the thinner fibers but their larger surface area would also allow for a better storage of the intercepted particles. It should be emphasized that the effect of the van der Waals forces can be felt by nanoparticles only at the distances $\sim$100 nm, and that is the reason of the predominant

![Fig. 11. Microscopic images of electrospun PAN filter membrane (with copper-plating) after filtration of airborne Al nanoparticles. The following positions at the membrane: (a) the center, (b) top, (c) bottom, (d) the left-hand side, and (d) right-hand side. The membrane was formed by electrospinning of the 10 wt % PAN solution in DMF. The average fiber size is $\sim$749 nm. The scale bars are 10 $\mu$m.](image1)

![Fig. 12. The binary image corresponding to the images in Fig. 10a–e, respectively. The luminance level is set to 0.45 for all the figures. The scale bars are 10 $\mu$m.](image2)
interception of nanoparticles by the thinner fibers [41]. On the other hand, the thicker fibers (~500 nm) displace airborne nanoparticles to the distances of ~500 nm (cf [41]), where the effect of the van der Waals forces is immaterial, and accordingly, the nanoparticle interception becomes less effective and could occur by means of only inertial forces and diffusion.

3.2. Effect of electric forces on filtration efficiency of the filter membrane comprised of thicker fibers

The effect of the van der Waals forces abruptly fades with a distance from the fiber center, and thus, thicker fibers (>~100 nm) displacing flow to distances comparable to their cross-sectional sizes, are incapable of nanoparticle interception by means of the van der Waals forces (cf. section 3.1 and [41]). As the inertial and diffusion-driven interception of the Al nanoparticles by the thicker fibers of ~500 nm is ineffective, the electric force might be expected to increase the interception efficiency of such fibers. This idea is corroborated by the results in [45–47].

Then, in the present work the filter membrane formed by electrospinning of the 10 wt % PAN solution in DMF for 3 min was employed. The solution feeding flow rate in electrospinning was 0.2 mL/h at the applied voltage of 7 kV–9 kV. The fibers were deposited on a rotating copper mesh located at a distance of 10 cm from the needle. The resulting average fiber size was measured as ~509 nm.

Another filter membrane was formed exactly as the above-mentioned one. After that, it was sputter coated with Pt and then, electroplated by copper for 40 s. The resulting average fiber size was measured as ~749 nm.

The filtration tests with airborne Al nanoparticles were conducted using the bare PAN and copper-plated PAN filter membranes and the identical rate of particle feeding of 0.22 mg nanoparticles per minute. The filtration tests lasted for 2 min for each filter membrane. The charged nanoparticles were intercepted by the grounded copper-plated membrane (cf. Fig. 5).

The optical images of the bare PAN filter membrane after nanoparticle filtration are shown in Fig. 10, while those the copper-plated one - in Fig. 11. In both cases, five images are randomly chosen from the center, top, bottom, left and right sides of the filter membranes to quantify the particle interception by the method described in section 2.5. The resulting binary images corresponding to those of Figs. 10 and 11 are shown in Figs. 12 and 13, respectively. The measured particle percentages relative to the area of each image in both cases are shown in Table 2. Note, that the total area of all images was the same. For the filter membrane with the fiber size of ~509 nm, with the electric force involved in the particle interception, the average particle percentage of 0.332% was measured. This value was almost twice the one measured for the bare PAN filter membrane, which is 0.188%. The result is in agreement with the optical observations and corroborates the method developed for the quantification. Note that for both filter membranes explored in the present section the effect of the van der Waals forces was immaterial, because both were comprised of fibers much larger than 100 nm in cross-section.

3.3. Filter membrane with combined effects of the van der Waals and electric forces

To combine and compare nanoparticle interception by means of the van der Waals and electric forces, one needs to form identical metal-
plated filter membranes with approximately the same cross-sectional
fiber sizes of ~100 nm. Electroplating significantly increases fiber size
(cf. section 3.2). The basic filter membrane would be electrospun from
the 6 wt % PAN solution in DMF, with the average fiber size of ~100 nm.
After copper-plating for 40 s, the fiber size increases dramatically, up to
more than 7 times, and becomes ~765 nm, as measured by ImagJ (cf.
Fig. 14a). Moreover, there are still fibers incompletely covered by Cu
during the 40 s plating, as is marked by red loops in Fig. 14b.

Therefore, in the present section metal-plating of fibers is achieved
by means of sputter coating by Pt alone, without any subsequent elec-

troplating of copper. Two identical filter membranes were electrospun
using the 17 wt % solution of Nylon 6 in 88% formic acid for 2 min. The
feeding rate of the solution was 0.05 mL/h at the applied voltage of 10
kV–12 kV and the needle-to-collector distance of 10 cm. The resulting
average fiber size was measured as ~80 nm, close to those reported in
[26,41]. Then, the filter membranes were sputter coated with 10 nm Pt
layer to metallize the fiber surfaces. The filtration experiments were
conducted with airborne Al nanoparticles supplied at the rate of 0.22 mg
nanoparticles per minute. Note that the concentration of Al nano-
particles in suspension was chosen such that the membrane after
filtration would be almost covered by nanoparticles, but not fully
clogged, which allows for a statistically sound analysis of the filtration
efficiency. In both cases, the fiber size after Pt-plating was <100 nm, i.e.,
the van der Waals force-driven particle interception was expected [26].
However, the interception could also be facilitated by the additional
electric forces. To achieve that, the oncoming Al nanoparticles were

Fig. 14. SEM images of electrospun filter membrane formed from the 6 wt % PAN solution in DMF and subsequently copper-plated for 40 s. (a) The majority of the
fibers are fully plated by Cu. (b) However, some fibers marked by red loops are not fully plated by Cu. The scale bars are 5 μm. (For interpretation of the references to
colour in this figure legend, the reader is referred to the Web version of this article.)

Fig. 15. Microscopic images of electrospun Nylon 6 filter membrane subsequently sputter coated with 10 nm of Pt. In the filtration experiment the ionizer was on,
and the membrane was grounded as in Fig. 5. Accordingly, filtration of Al nanoparticles was driven simultaneously by the electric and van der Waals forces. The
following positions at the filter: (a) the center, (b) top, (c) bottom, (d) the left-hand side, and (d) right-hand side. The scale bars are 10 μm.
negatively charged by the ionizer, whereas the filter membrane was grounded (cf. Fig. 5). When the ionizer was on, the nanoparticle interception was driven by simultaneously acting electric and van der Waals forces (Fig. 15). On the other hand, when the ionizer was off, the nanoparticle interception was driven by the van der Waals forces alone (Fig. 16). The images shown in Figs. 15 and 16 were transformed to the binary mode in Figs. 17 and 18, respectively, as in section 3.2.

The resulting percentages of particle coverage of the filter area in the images in Figs. 17 and 18 are listed in Table 3. The average percentages of particle area with the ionizer being on (i.e., with the electric and van der Waals forces acting simultaneously) is 0.47%. This value is practically twice the one measured with the ionizer being off, 0.21%, (i.e., with the van der Waals forces acting alone). The results reveal that filter membranes intercepting nanoparticles by the electric and van der Waals forces acting simultaneously are feasible, and provide an enhanced efficiency.

In addition, compared to the average particle percentage area of 0.332% obtained with electroplated thicker fibers intercepting nanoparticles by means of the electric force in section 3.2, the present percentage of 0.47% reveals a positive effect of the interception by the...
Note also that the pressure drop on the filter membranes formed from the 17 wt % Nylon 6 solution in 88% formic acid, measured by a MATK-186 Digital Manometer from Tekcoplus, was $\Delta P = 0.06 \pm 0.001$ psi. Then, because the average coverage of a membrane by particles can be considered as a measure of the filter efficiency $E$, Eq. (2) yields the quality of the filter in Fig. 16 as $Q_F = 10.6$ psi$^{-1}$ and that of the one in Fig. 17 as $Q_F = 3.9$ psi$^{-1}$. That means that the quality of the membrane with the coupled action of the van der Waals and Coulomb forces is almost three times the one without the electric Coulomb force.

### 4. Conclusion

The present work aims at the most effective way of filtering airborne nanoparticles arising from airborne water drops loaded with the approximately COVID-19 virus-sized nanoparticles ($\sim 100$ nm in the present case). The droplets fully evaporate in flight resulting in airborne virus-like nanoparticles (the situation resembling that in reality).

(i) The effect of the van der Waals forces, which is significant in the interception by the $\sim 100$ nm nanofibers, was responsible for a higher filtration efficiency of such nanofibers compared to the fiber membrane comprised of fibers of $\sim 500$ nm in cross-section. Accordingly, filter membranes incorporating layers of $\sim 100$ nm nanofibers could be highly effective in the interception of $\sim 100$ nm nanoparticles by means of the van der Waals forces.

(ii) The effect of the electric forces on the interception of pre-charged (in flight through an ionizer) nanoparticles by the membranes comprised of 500–700 nm electrospun nanofibers (metal-plated (with electric field) and non-metal-plated (without electric field)) was elucidated. It was shown that the efficiency was increased by the factor of $0.332/0.188 = 1.77$ due to the electric forces-facilitated interception.

(iii) It was shown that it is possible to combine the positive effects of the van der Waals and electric forces in filter membranes with nanofiber sizes of $\sim 80$ nm, which were sputter coated with Pt layer of $\sim 10$ nm. In such a case, the electric forces increase the filtration efficiency by the factor of $0.47/0.21 = 2.24$ compared to the van der Waals forces alone. Compared to the filter membranes with $\sim 500$ nm fibers without the electric field, the combined van-der-Waals-electric filter membrane with fibers $\sim 90$ nm is $2.24 \times 1.77 = 3.96$ times more effective.

(iv) The quality factor of a membrane which combines the van der Waals and Coulomb forces is almost three times that of a comparable membrane without the electric Coulomb force (with only van der Waals forces).

(v) In the present work electrospun Nylon 6 and PAN nanofibrous membranes were used as model filter materials. Cellulose fiber-based filters would also be of significant interest in practical applications. Electrospinning of biopolymer solutions, and in particular, cellulose solutions is also possible [25,27,55]. It should be emphasized that electrospinning of cellulose solutions in the Schweizer’s reagent, yields nanofibers in the 100–300 nm range [55], and a further reduction of fiber size seems to be possible. Therefore, cellulose nanofibrous membranes could also incorporate the van der Waals-based filtration demonstrated in the present work. To incorporate an additional electric force by means of metal coating, while still being able to benefit from the van der Waals forces, one needs to avoid a significant increase in the fiber diameter. This can be achieved, as in the present work, by means of sputter coating, which also eliminates the need in

### Table 3

| Figure number | With (or without) the electric forces | Luminance level | Particle area % | Average particle area % |
|---------------|---------------------------------------|-----------------|-----------------|-------------------------|
| 17a           | Yes                                   | 0.35            | 0.16            |                         |
| 17b           | Yes                                   | 0.35            | 0.38            |                         |
| 17c           | Yes                                   | 0.35            | 0.42            |                         |
| 17d           | Yes                                   | 0.35            | 0.65            |                         |
| 17e           | Yes                                   | 0.35            | 0.76            | 0.47                    |
| 18a           | No                                    | 0.30            | 0.05            |                         |
| 18b           | No                                    | 0.30            | 0.41            |                         |
| 18c           | No                                    | 0.30            | 0.15            |                         |
| 18d           | No                                    | 0.30            | 0.23            |                         |
| 18e           | No                                    | 0.30            | 0.21            | 0.21                    |

Fig. 18. The binary images corresponding to those in Fig. 16a–e, respectively. The luminance level was set to 0.3 for all figures. The scale bars are 10 μm.
electroplating and thus, in part, negative environmental consequences of manufacturing of cellulose nanofibrous membranes.

Author statement

Kailin Chen: Methodology, Software, Formal analysis, Investigation, Writing – Original Draft, Writing – Review & Editing, Visualization. Jingwei Wu: Methodology, Investigation, Writing – Original Draft, Visualization.

A.L. Yarin: Conceptualization, Validation, Writing – Original Draft, Writing – Review & Editing, Supervision.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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