

Preparation of Electrospun PVDF Nanofiber Composite Filter Medium and Its Application in Air Filtration

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Abstract: Nanofibrous media with both high particle interception efficiency and robust air permeability has broad technological applications in areas including individual protection, industrial security, and environmental governance. However, producing such filtration media has proven to be extremely challenging. Here we reported an approach to preparing and fabricating a polyvinylidene fluoride (PVDF) nanofiber composite filter medium composed of 2D PVDF nanofiber nets and a stable substrate via one-step electrospinning for effective air filtration. PVDF nanofibers are obtained by adjusting the electrospinning process. With the combined properties of ultrasmall diameter, high porosity, and a bonded scaffold, the resulting PVDF nanofiber composite filter medium exhibits a robust high filtration efficiency of 99.901% (equivalent to an F9 rating) for 0.4 μm particles and a long service life (a large dust holding capacity of 36 g/m^2) for ultrafine airborne particles based on the sieving principle and surface filtration behavior. The successful synthesis of PVDF nanofibers medium would not only make it a promising candidate for air filtration, but also provide new insights into the design and development of composite nanofiber structures for various applications.

Keywords: electrospinning; filtration efficiency; nanofiber; dust holding capacity; air filtration

1 Introduction

Fiber Filters, which are widely used in air filtration, are attractive for particle filtration owing to their cost-effectiveness and ease of scalable synthesis from various materials^[1-2]. When fibrous media is used for air filtration, two factors generally



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need to be considered. One is the fiber diameter, which determines the filtration efficiency of the filter medium^[3-4]; the other is the filter medium's structure, which affects the air permeability of the medium and reduces the energy cost^[2, 5].

Nanofiber-based filtration media is currently attracting increasing attention because it can enhance the filtration performance (especially the filtration efficiency)^[6-7]. There are many techniques for making nanofibers, such as template synthesis^[8], sea-island spinning^[9], phase-separation^[10], plasma treatment^[11], and electrospinning^[12]. Compared with other technologies, electrospinning has become the most effective method for the preparation of ultrafine fibers^[13-14] owing to its simple equipment, easy operation, and sustainable production. In recent years, with the development of electrospinning technology, hundreds of polymers have been prepared as nanofiber materials by electrospinning^[15-16], e.g., polyacrylonitrile (PAN)^[17], PAN/poly(acrylic acid)^[18], polyetherimide^[19], poly(lactic acid)^[20], and polyamide-66 (PA-66)^[21]. However, these materials still have some disadvantages: inadequate filtration performance, weak mechanical properties, and short service life.

Polyvinylidene fluoride (PVDF) is attractive for electrospinning owing to its combined properties of flexibility, low weight, low thermal conductivity, high chemical corrosion resistance, and heat resistance. In this study, PVDF was used as a spun polymer to prepare nanofibers, which were incorporated into a substrate. To improve the filtration performance (especially the filtration efficiency and dust-holding capacity (DHC)) of the filter medium, the effect of the electrospinning parameters on its performance and the effect of the electrospun PVDF nanofibers on the filtration performance of air filters were investigated.

2 Experimental

2.1 Raw materials

PVDF powder ($M_w=300000$) was purchased from Solvay (Shanghai) Co., Ltd., N,N-dimethylformamide (DMF) and acetone were purchased from Sigma-

Aldrich Chemical Co. (St. Louis, MO, USA). Bilayer composite air filter paper (120 g/m^2) was supplied by our laboratory as the substrate to receive the electrospun PVDF nanofibers. All chemicals were of analytical grade and were used as received without further purification.

2.2 Preparation of PVDF solutions

A preliminary study found that a spinning solution consisting of PVDF powder dissolved in a mixed solvent system of DMF and acetone is most suitable for electrospinning. It was found that when the volume ratio of DMF and acetone was 2 : 3 and the mass fraction of PVDF in the spinning solution was 12 wt%, PVDF nanofibers with better quality could be obtained.

The PVDF powder was first dissolved in DMF at a certain concentration and stirred at 40°C for 4 h until a transparent homogeneous solution was obtained. Then, the PVDF/DMF solution was cooled to room temperature, and a calculated amount of acetone was added. The volume ratio of DMF and acetone in the resulting PVDF/DMF/acetone solution was 2 : 3. The blended PVDF/DMF/acetone solution was stirred for another 2 h to ensure complete dispersion of PVDF in the solvent.

2.3 Fabrication of PVDF nanofibers

PVDF nanofibers for deposition on the bilayer composite air filter substrate were fabricated using FM-1205 spinning equipment (Beijing Future Material Sci-tech Co., Ltd., China). A schematic diagram of the electrostatic spinning process and nanofiber composite air filter medium is shown Fig.1.

To electrospin PVDF fibers, the PVDF/DMF/acetone solution was placed in a 10 mL plastic syringe equipped with a stainless steel needle as the spinneret. A digitally controlled syringe pump was used to feed the polymer solution into the needle tip at a constant feeding rate of 0.005 mm/s. A metal roller wrapped in bilayer composite filter paper was electrically connected to the negative high-voltage DC power supply and used as the fiber collector. A stainless steel needle with an inside diameter of 0.4 mm was

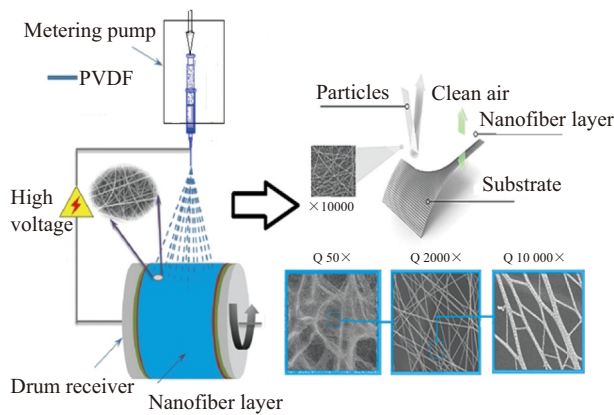


Fig.1 Schematic diagram of electrostatic spinning process and nanofiber composite air filter medium

electrically connected to the positive high-voltage DC power supply. During the electrospinning process, the PVDF solution was exposed to a high DC electrical field, which was generated by applying a positive voltage of 27 kV and a negative voltage of 3 kV to a 15 cm gap between the spinneret and the fiber collector. The ambient temperature was 35°C, and the relative humidity was kept at 35%. After electrospinning, a nonwoven nanofibrous PVDF membrane was formed on the bilayer composite air filter paper. The obtained nanofiber composite air filter medium was then dried in vacuum at 60°C for 4 h to remove the residual solvent before any further characterization.

2.3 Characterization

2.3.1 Pore size of nanofiber composite air filter medium and diameter of PVDF nanofibers

The morphology of the nanofiber composite air filter medium was examined by scanning electron microscopy (SEM) (S-3400N, Hitachi Ltd., Japan) after the medium was coated with gold. The fiber diameter of each PVDF nanofiber layer was measured by an image analyzer (Image-Pro Plus 6.0), and the pore size of the PVDF nanofiber layers was obtained by analyzing a series of SEM images using the grid method.

2.3.2 DHC, filtration resistance and filtration efficiency

The filtration performances of all the air filter materials with developed pore structure were measured using a filtration test bench^[15]. The measurement protocol

was based on the ISO 5011 international standard for evaluating the basic performance characteristics of inlet air cleaning equipment for internal combustion engines and compressors. The results were compared and analyzed. An in-house-developed bench was used for the filtration tests, and the test conditions are shown in Table 1. Dust was fed through the filtration chambers using a compressed air particle disperser. The particle size distribution of fine dust is plotted in Fig.2.

The test bench (Fig.3) is composed of two filtration chambers:

(1) The tested filter is placed inside the first chamber (upstream chamber), which contains flowing air charged with dust before filtration.

(2) A high-efficiency particulate air filter is placed inside the second chamber (downstream chamber) to collect the fine dust particles that cross the tested filter and reach the chamber.

The measured filtration properties are the pressure drop, fractional filtration efficiency, and DHC. The DHC is the quantity of captured particles inside the tested filter; the difference between the initial and final

Table 1 Test conditions for nanofiber composite air filter medium

Test dust	ISO 12103-A2
Dust concentration/(g · m ⁻³)	1
Face velocity/(L · min ⁻¹)	60
Test area/cm ²	100
Test terminal condition/Pa	450

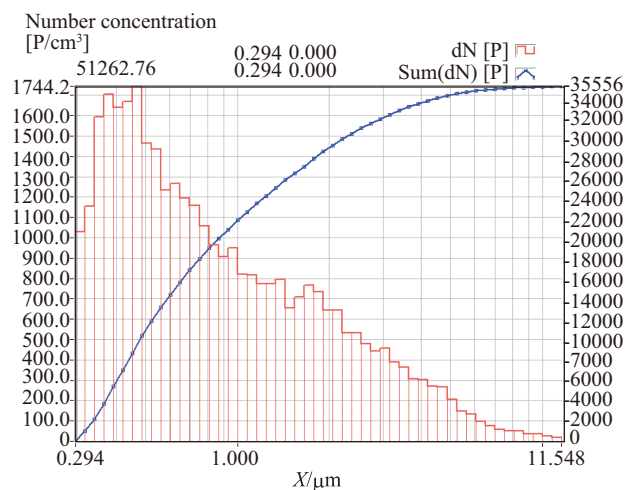
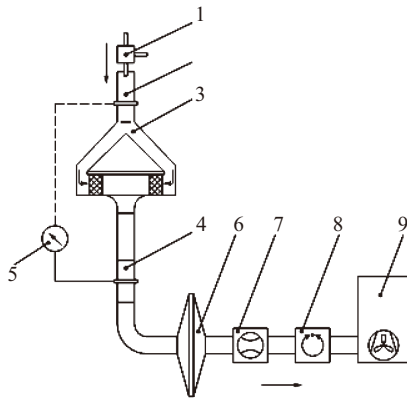


Fig.2 Fine dust particle size distribution



1—Dust injector; 2—Inlet tube; 3—Test shroud; 4—Outlet tube; 5—Pressure measuring device; 6—Absolute filter; 7—Air flow meter; 8—Air flow control; 9—Exhauster

Fig.3 Experimental set-up of the filtration test bench

weights of the tested element gives the DHC in g/m^2 . Thus, the DHC is obtained using Equation(1).

$$\text{DHC} = (M_2 - M_1) / A \quad (1)$$

Where, M_1 is the initial weight of the test element, M_2 is the final weight of the test element, and A is the test area of the tested filter.

3 Results and discussion

3.1 Characterization of PVDF nanofibers

In this study, PVDF nanofibers of nearly uniform diameter were successfully produced by controlling the PVDF/DMF/acetone electrospinning solution, DC voltage (30 kV), and receiving distance (15 cm). The organic solvent acetone was added to decrease the viscosity and surface tension of the electrospinning solution owing to its low viscosity and low density. Representative SEM micrographs of PVDF nanofibers obtained using various electrospinning times are shown in Fig.4(a)~Fig.4(c). The images reveal randomly oriented nonwoven scaffold structures that support ultrathin 2D nanonets.

The diameter distribution of the PVDF nanofibers is shown in Fig.4(d). It can be seen that under

the experimentally determined process parameters, the diameter of the electrospun PVDF nanofibers is distributed between 60 nm and 350 nm, and falls mainly between 60 nm and 150 nm. Fibers in this range account for nearly 80% of the total, whereas fibers with diameter of 150~350 nm account for only about 20%. This shows that PVDF nanofibers with a smooth morphology and small diameter can be obtained under the spinning conditions determined in this study.

The number of nanofibers in the PVDF layer could be controlled by varying the electrospinning time. This method seems to be suitable for mass production. As shown in Fig.4(a)~Fig.4(c), the density of nanofibers in the PVDF layer gradually varied from sparse to dense as the electrospinning time increased. For a short time of 5 min, as shown in Fig.4(a), only a small quantity of PVDF nanofibers was deposited onto the substrate. However, when the electrospinning time was extended to 10 min, as shown in Fig.4(b), the number of PVDF nanofibers on the substrate increased significantly, and they formed a simple network structure. When the electrospinning time was further increased to 15 min, as shown in Fig.4(c), a dense nanofibrous PVDF layer with a complex network structure, indicating

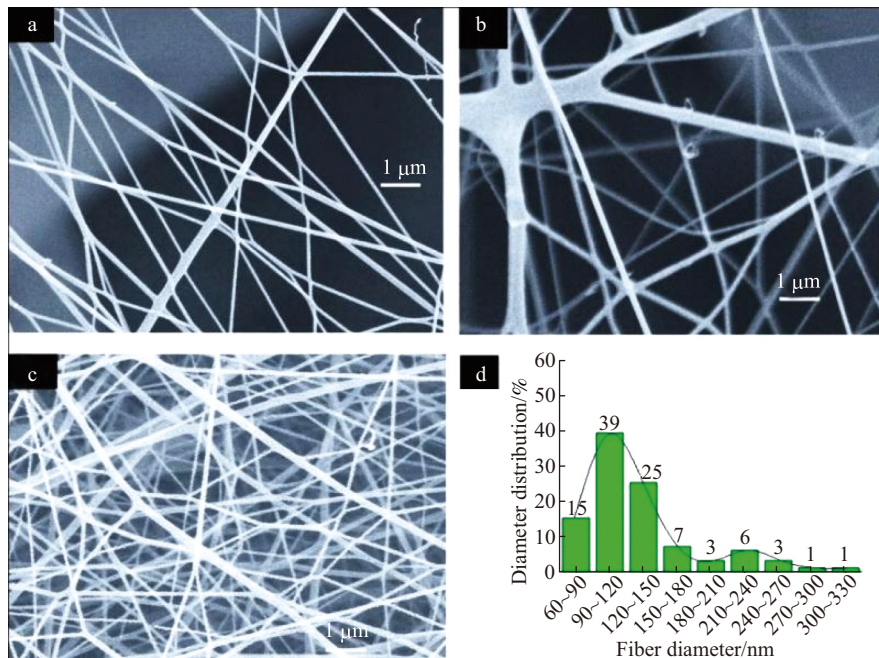


Fig.4 SEM micrographs of nanofibrous PVDF layers produced at electrospinning times of (a) 5 min, (b) 10 min, (c) 15 min and (d) the diameter distribution of the PVDF nanofibers

good filtration performance for fine dust particles, was formed on the substrate.

3.2 Pore structure of PVDF nanofiber layer

The pore structure was examined by measuring the pore size and pore size distribution using the grid method to investigate the effect of the electrospinning time on the structure of the nanofibrous PVDF layer, and thus to reveal the unique superiority of the nanonets and cavity structures for airborne particle filtration. Fig.5 shows the pore diameter and pore size distributions of the nanofibrous PVDF layers formed using various electrospinning times. The results show that the pore size distribution of the nanofibrous PVDF layers gradually changes from wide to narrow as the electrospinning time increases from 5 min to 15 min.

Fig.5(a)~Fig.5(c) show that as the electrospinning time increases, the pore size distribution of the electrospun PVDF fiber layer is first dispersed and then concentrated. As shown in Fig.5(a), when the electrospinning time is 5 min, the pore size distribution of the electrospun PVDF fiber layer is between $0.43\ \mu\text{m}$ and $5\ \mu\text{m}$, and the distribution is relatively broad; when the electrospinning time increases to 10 min, as shown in Fig.5(b), the pore size distribution becomes narrower, and the pore size is continuously distributed in the low-diameter region. When the electrospinning time is 15 min, as shown in Fig.5(c), the pore size distribution is concentrated between 0 and $1.5\ \mu\text{m}$. Fig.5(d) shows that as the electrospinning time increases, the maximum, minimum, and average pore diameters of the PVDF nanofiber layers decrease. When the electrospinning time increases from 5 min to 15 min, the

maximum diameter decreases from $4.9\ \mu\text{m}$ to $1.5\ \mu\text{m}$, the minimum diameter decreases from $0.4\ \mu\text{m}$ to $0.2\ \mu\text{m}$, and the average diameter decreases from $1.0\ \mu\text{m}$ to $0.7\ \mu\text{m}$. The reason is that as the electrospinning time increases, the number of fibers in the nanofiber layer increases gradually, and the fibers are deposited more densely. The small pore size structure, in which the particulates form a filter cake on the surface of the filter material and achieve surface filtration, enables the filter medium to remove particulates from polluted air.

3.3 Influence of electrospinning time on the filtration efficiency

The filtration efficiency of the PVDF nanofiber composite air filter media fabricated using various electrospinning times under a face velocity of $60\ \text{L/min}$ is demonstrated in Fig.6. The filtration efficiency of the nanofiber composite air filter materials versus

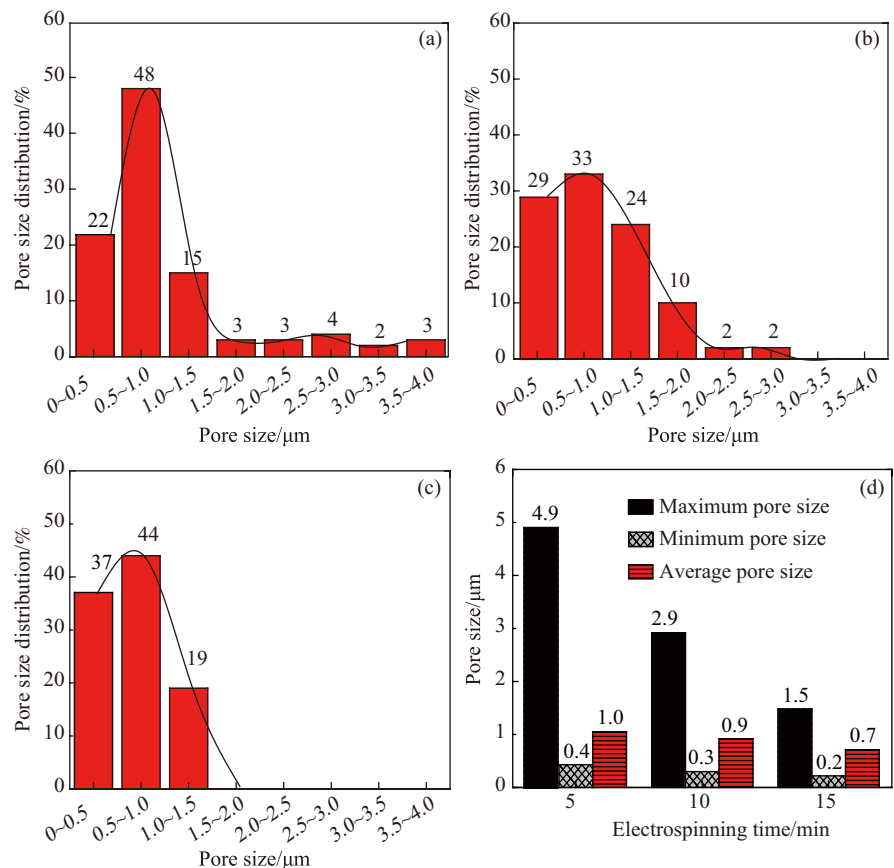
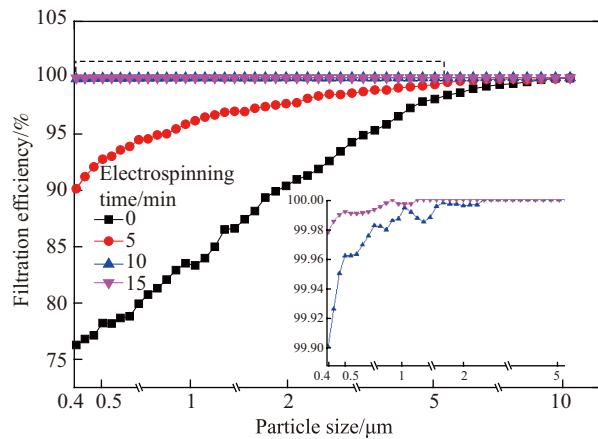


Fig.5 Pore size distributions of nanofibrous PVDF layers fabricated using various electrospinning times of (a) 5 min, (b) 10 min, and (c) 15 min, and (d) distributions of the maximum, minimum, and average pore sizes



Note: electrospinning time of 0 indicates that no PVDF nanofibers are combined with the substrate (blank sample).

Fig 6 Filtration efficiency of PVDF nanofiber composite filter media fabricated using various electrospinning times

the electrospinning time (5, 10, and 15 min), which controlled the number of PVDF nanofibers, improved to varying degrees when the electrospinning time increased to 15 min. Obviously, the filtration efficiency exhibited a sharp rise for particle sizes of $\leq 5 \mu\text{m}$ but improved slightly for particle sizes of $\geq 5 \mu\text{m}$.

The filtration efficiency of the substrate for $0.4 \mu\text{m}$ particles was only 76.275% when the PVDF nanofibers were not reassembled on the substrate. However, when PVDF nanofibers were incorporated into the substrates by electrospinning, the filtration efficiency of the nanofiber composite air filter materials with electrospinning times of 5, 10, and 15 min were 90.144%, 99.901%, and 99.978%, respectively. Obviously, the filtration efficiency was greatly improved and reached a relatively steady value when the electrospinning time was 10 min, and it could easily meet the standard for high-efficiency particulate air filters ($>99.97\%$) when the electrospinning time was 15 min; traditional filters cannot meet this standard, therefore this result further reveals the key role of the nanofibers and multilayer composite structures in air filtration.

3.4 Influence of electrospinning time on DHC

To judge the quality of filter materials, it is generally necessary to consider their overall filtration performance. The filtration efficiency is not the only

evaluation parameter for judging the quality of filter materials. In fact, when fibrous media are used for air filtration, two factors need to be considered. One is the filtration efficiency, which determines the quality classification of filter materials; the other is the DHC, which can indirectly reflect the service life of filter materials. Therefore, in the following, the influence of electrospinning time on the filter medium's DHC is investigated. Consequently, the relationship between the electrospinning time and the DHC of the fibrous medium is examined, and the qualitative and quantitative effects of the DHC are clearly demonstrated.

The influence of the electrospinning time on the DHC is shown in Fig.7. The highest DHC is obtained for the substrate without PVDF nanofibers owing to its internal structure with many large pores, which allows particles to be deposited in the pores of the filter medium without rapidly clogging them. Although the substrate has a high DHC, its filtration efficiency is very low. Therefore, it cannot satisfy the requirements for high-efficiency filtering.

The DHC of the PVDF nanofiber composite filter medium decreased with electrospinning time. For electrospinning times of 5, 10, and 15 min, the DHC of the PVDF nanofiber composite filter medium decreased to 41, 36, and 34 g/m^2 , respectively. In fact, each fiber type affects the medium filtration ability as well as contributing to the mechanical behavior of the filtration structure. The fine fibers make an essential contribution to the particle capture improvement. The decrease in the fiber diameter results in a higher number of fibers for an equivalent filter medium packing density, which increases the statistical probability that dust particles encounter fibers. This increase potentially leads to an improvement in the filtration behavior, as shown in Fig.6. However, as the electrospinning time increases, the number of fibers in the nanofiber layer gradually increases, and the fibrous arrangement becomes increasingly compact. This fibrous arrangement causes clogging at the interface between the PVDF nanofibers and the substrate layer, which quickly increases the pressure drop and thus reduces the DHC of the medium

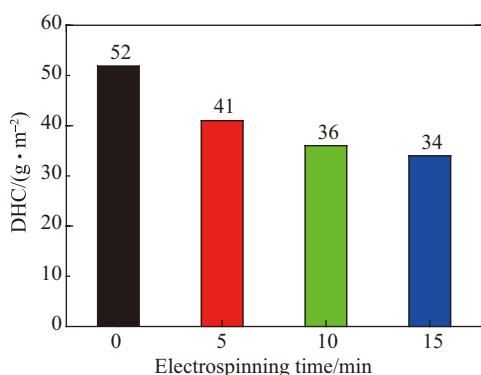


Fig.7 DHC of PVDF nanofiber composite filter media fabricated using various spinning times

significantly despite its good filtration efficiency.

To improve the filtration performance of fibrous media, the DHC and the filtration efficiency must be balanced. When the electrospinning time was 10 min, the nanofiber composite filter material had high filtration efficiency and high DHC, which can meet the requirements for high-efficiency filtration.

4 Conclusion

In summary, we designed and fabricated PVDF nanofiber composite filter media composed of 2D PVDF nanofibers and a stable substrate for effective air filtration via one-step electrospinning. PVDF nanofiber formation is promoted by adjusting the electrospinning process. When the volume ratio of DMF and acetone is 2 : 3, the mass fraction of PVDF in the spinning solution is 12%, the acceptable distance is 15 cm, the electrospinning time is 10 min, and the spinning voltage is 30 kV, the PVDF nanofibers with smooth morphology and stable size can be obtained. With combined properties of ultrasmall diameter, high porosity, and a bonded scaffold, the resulting PVDF nanofiber composite filter medium exhibits a robust high filtration efficiency of 99.901% (equivalent to an F9 rating) for 0.4 μm particles and a long service life (large dust holding capacity of 36 g/m^2) for ultrafine airborne particles based on the sieving principle and surface filtration behavior.

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