Electrospinning with a spindle-knot structure for effective PM_{2.5} capture

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ABSTRACT Long-term air contamination and pollution challenges in particulate matter (PM) have raised fervent concerns for public health, e.g., the PM physical damage or the bacteria and virus carried by the PM. The desired air filter, seeking both high filtration efficiency and low pressure drop remains challenging. Here, we report a bio-inspired spindle-knot halloysite nanotube microsphere-incorporated nanofiber (HNM-NF) filter with the assembly and shape structures of the spider silk. The resulting HNM-NFs exhibit integrated properties of high surface energy, hydrophilicity and strong PM capture. The spindle-knot structures could shrink the outer pore size on two-dimensional (2D) surface and construct the fluffy 3D reticular architecture, facilitating high-efficiency air pollutant capture (>85.0%) while maintaining low resistance to airflow (~39 Pa). The spindle-knot construction method was applicable to various materials (i.e., Al₂O₃, ZnO and TiO₂) and volume production of the microsphere-incorporated NF cartridge. The diversified spindle-knot construction will be valuable for adapting to meet different filtration requirements.

Keywords: spindle knot, electrospinning, bio-inspired, PM_{2.5}, air filter

INTRODUCTION

Air pollution is one of the most severe urban problems, mainly due to industrial exhaust emissions and secondary inorganic aerosols [1–4]. PM_{2.5} (particulate matter with the size below 2.5 μm) emissions have very serious long-term influences on climate, air quality and human health, especially cardiac and respiratory systems [5,6]. Electrospun air filter is a potential technique to address the above problem, and an effective architecture offering high-efficiency air pollutant capture, while maintaining

low resistance to airflow is the key to success [7,8].

Multiple electrospun precursor solutions, a series of components and their combinations, such as polymers (e.g., polyurethane, polyacrylonitrile and polyamide-6) [9] and ceramics (e.g., SiO₂, ZrO₂ and CeO₂), have been used to fabricate nanofiber (NF) filters [10–13]. The related studies demonstrated that PM_{2.5} particles are collected on the filter mainly by inertial impaction, interception and Brownian diffusion [14]. Various efforts have been made to design and fabricate effective PM_{2.5} filters based on the structures and surface properties. One of the effective strategies is functionalization or polarization of NFs, such as polar polymeric NFs, Ag nanowire percolation networks and magnetic nanoparticle-decorated NFs [5,14,15]. However, the fabrication of these NFs requires expensive raw materials and complex application conditions (e.g., an extra electric field or magnetic field).

Numerous secondary microstructures, including porous, hollow and core-sheath structures, have also been constructed on NFs to enhance PM_{2.5} particle capture [16–18]. Nonetheless, NFs with the characteristics of light weight, large surface areas and abundant pore hierarchy are also accompanied with compromised mechanical strength, thus impairing their durability and service life. For solving this problem, several composite structures of electrospun membrane filters have been developed, including layer-by-layer constructs, self-assembled two-dimensional (2D) nanoarchitecture networks and metal-organic frameworks [19–23,24]. However, high filtration resistance and complex fabrication processes have been the main drawbacks in practical applications. Consequently, a long-standing pursuit is to design a high-efficiency structure with a convenient preparation technology

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to create air filters with low filtration resistance.

Here, inspired by dust capture by spider silk [25–27], spindle-knot NFs with halloysite nanotube microsphere (HNM) were prepared by spray-drying and electrospinning (Fig. 1a). The surface pores formed by NFs weaving in 2D pattern and the inner fluffy 3D reticular architecture play different roles in $PM_{2.5}$ capture and dust holding [28]. In this study, the morphologies (fiber diameter and spindle-knot density) and porosity of the filters were tuned to optimize the air filtration performance. The best mass ratio of microspheres is 7 wt%; with this content, the HNM-NF filter exhibits a high specific surface

area, large pore volume, optimal spindle-knot density and hydrophilic surface, resulting in a more effective and stable air filtration performance under ultra-low filtration resistance. More importantly, large HNM-NF filters with a size of $0.66\text{ m} \times 15\text{ m}$ were fabricated and then successfully used for volume production of HNM-NF filter cartridge.

EXPERIMENTAL SECTION

Materials

Halloysite nanotubes (HNTs) with length ranging in 300–

Figure 1 Fabrication, characteristics and air filtration of the HNM-NF filters. (a) Schematic of the differences between spider silk and bio-inspired electrospinning NF on microstructure and single spindle knot. (b) Schematic illustrations of the preparation process of HNM-NF filter: (I) construction of the self-assembled spray-dried HNMs. Scale bar, $5\text{ }\mu\text{m}$. (II) Fabrication of the HNM-doped electrospinning solutions; (III) the one-step electrospinning process. (c) SEM images of 0, 5, 7, 9 and 11 wt% HNM-NF filters, respectively. Scale bars, $20\text{ }\mu\text{m}$. (d) The size distributions of the HNM-NFs in (c) with normalized curves. (e) Photographs of HNM-NF strips with different extents of *in situ* twisting. Scale bars, 10 cm . (f) Schematic showing the set-up for the measurement of pressure drop of the HNM-NF filters. (g) $PM_{2.5}$ η of HNM-NF filter under various humidity levels.

800 nm, inner diameter ranging in 10–30 nm and outer diameters ranging in 40–150 nm were provided by Chenxi, Hunan province, China. Polycaprolactone (PCL) was supplied by Sigma-Aldrich. Trifluoroethanol was purchased from Hunan Hongjie Chemical Technology Co., Ltd. TiO₂ nanoparticles (NPs) with an external diameter of 50–100 nm were purchased from Kurt New Materials Technology Co., Ltd. ZnO NPs, which had diameters in the range of 50–100 nm, were supplied by Shanghai Yaoyi Alloy Material Co., Ltd. Al₂O₃ NPs with diameters in the range of 50–100 nm were purchased from Shanghai Xinzuan Alloy Material Co., Ltd.

Preparation of HNMs

The homogeneous HNTs were prepared through purification and classification processes as described in a previous report [28]. The HNT solution was prepared by mixing 10.0 g of HNTs in 30.0 g of deionized water (with a weight ratio of 1:3) under continuous stirring at 600 r min⁻¹ for 1 h. Then, the solution was spray-dried (Mini Spray Dryer, Type YC-500, China) through a 1.0-mm nozzle to form crosslinked HNT microspheres by feeding the solution with a constant rate of 2 mL min⁻¹ through a programmable peristaltic pump with an inlet temperature of 180°C. To form compact microspheres, the HNT microspheres were calcined in a muffle furnace at 550°C for 2 h. Subsequently, the HNT microspheres were suspended homogeneously in deionized water, and the solutions were then allowed to naturally deposit for 3 min to remove the large size microspheres, and centrifuge at a rate of 10,000 r min⁻¹ to remove the ultra-small microspheres. Finally, the obtained narrow-scale homogeneous HNT microspheres were dried in an oven at 80°C overnight.

Preparation and volume production of spindle-knot filters

PCL (number-averaged molecular weight $M_n=80,000$; Sigma-Aldrich) was dissolved in trifluoroethanol (weight ratio of 1.5:8.5) at room temperature and stirred for 2 h to prepare the electrospinning solution. The PCL solution viscosity and conductivity were 303 mPa s and 26 $\mu\text{S cm}^{-1}$. Even though the viscosity and conductivity were affected by PCL solution and the addition amount of HNMs, a small amount (weight ratio ≤ 11 wt%) of HNMs showed undetectable influence on solution viscosity and conductivity, verified by the HNM-NF filter fabrication and cartridge volume production. The HNT microspheres (with diameters ranged 2–5 μm) were added to prepare HNM/PCL solutions with HNM mass ratio of 0, 5, 7, 9 and 11 wt%. The electrospinning solu-

tions were prepared by ultrasonic dispersion to avoid HNM agglomeration and were continuously stirred at room temperature until a homogeneous mixture was obtained. The solution was loaded in a 10-mL syringe capped with a 19 G needle tip in the electrospinning device (YFSP-T, Yunfan Technology). The solution feed rate was precisely controlled with a syringe pump at a constant velocity of 2 mL h⁻¹. An optimized voltage of 14 kV was applied to promote the generation of a continuously charged electrospinning jet. The electrospun NF filters were collected on roller (100 r min⁻¹) covered in aluminium foil with a 15-cm distance from tip to collector. The volume production of large-scale HNM-NF filters and filter cartridges was processed by large scale multi-needles electrospinning machine MF01-001 (Foshan Lepton Precision Measurement and Control Technology Co., Ltd.).

Filter efficiency measurements

The representative particles with various compositions (e.g., sulfates, nitrates and organic carbon) and sizes were used to evaluate the filtration performance, generated by burning incenses. All of the filter efficiency measurements were tested in the lab under high levels of PM_{2.5} ($\sim 300 \mu\text{g m}^{-3}$), and each initial concentration was record for each HNM-filter then was used to calculate PM_{2.5} removal efficiency [29]. The initial values of stable PM injection ($\sim 300 \mu\text{g m}^{-3}$) were detected continuously and then gradually declined with the filter placed on the air inlet. The quick and dramatic evolution of filtration efficiency (η) was exactly recorded from low to high during the whole measurement. Requirements and test methods referred to ISO16890 [1,29]. The representative PM environment for 24-h test, which is full of automobile exhaust particles and road dust, was used to investigate the PM_{2.5} filtration performance of the HNM-NF filters in reality [5], on the South Lushan road (in Changsha, China). The concentrations of the test particles with and without the filters were measured using a particle counter (SDL307, Nuofang Electronics). The removal efficiency was simply calculated by comparing the concentration before and after filtration. We performed filtration performance tests of the filters at various humidity levels (30, 40 and 50 wt%). The pressure drop of each filter was measured by a differential pressure gauge (G505, Benetech Test Instrument). The wind velocity was tested by an anemometer (AS8336, Xima Electronics).

Characterizations

The scanning electron microscopy (SEM) images and

energy-dispersive X-ray spectroscopy (EDX) were examined by a Mira3 LMU SEM (Tescan, Czech Republic). The transmission electron microscopy (TEM) images and mapping analyses were collected with a Titan G2 60-300. X-ray diffraction (XRD) measurements of particles and NF filter samples were obtained by Rigaku TTR III. The water contact angle measurements and wettability evolution of the HNM-NF filters were tested with a contact angle goniometer (JY-82C, Chengde Dingsheng Testing Machine Testing Equipment Co., Ltd.). The Fourier transform infrared (FTIR) spectra were measured using a Shimadzu FTIR 8120 spectrometer over the range of 400 to 4000 cm^{-1} . The Brunauer-Emmett-Teller (BET) surface area was examined by a Micromeritics ASAP 2020 PLUS, USA. Focused ion beam (FIB) analyses were examined by an FEI Helios Nanolab G3 UC, USA.

RESULTS AND DISCUSSION

Design and filtration performance of HNM-NF filter

The spindle-knot-like HNM-NF was facilely prepared with the following three steps (Fig. 1b): (i) HNMs with appropriate size was firstly prepared by a spray-drying process as the raw materials for spindle knots; (ii) spindle knots were evenly distributed with ultrasonic dispersion and agitation; (iii) NFs with spindle knots were prepared by a direct electrospinning without exceptionally high voltage. The parameters for HNM spray-drying and electrospinning were explored to satisfy the requirements in Fig. S1. To verify the spindle-knot structures, the prepared filters were observed with environmental SEM, as shown in Fig. 1c. All the surface morphologies of the fibers were smooth and continuous, whereas spindle-knot structures were observed clearly on the HNM-NFs. The representative 0 and 7 wt% HNM-NF filters were investigated by SEM with various magnifications, as shown in Fig. S1d. There are numerous spindle knots dispersed on not only the outer surface but also the inner fluffy architecture of the HNM-NF filter. Compared with the PCL filter (0 wt%), the 7 wt% HNM-NF filter showed that a large amount of spindle knots were dispersed evenly throughout the whole filter under low magnification, and the spindle-knot structures and morphologies could be clearly observed with high magnification.

In Fig. 1d, the results of HNM-NF size distribution exhibit monomodal distribution curves, consistent with the SEM images. The diameters of HNM-NFs (5, 7 and 9 wt% relative to HNM ratio) were mainly centered in a narrow range (especially 7 wt%), and the mean diameters of the HNM-NFs (5 wt%, $1.21 \pm 0.26 \mu\text{m}$; 7 wt%, $0.96 \pm$

$0.23 \mu\text{m}$; and 9 wt%, $1.09 \pm 0.27 \mu\text{m}$) were larger than that of the pure PCL NFs (0 wt%, $0.87 \pm 0.18 \mu\text{m}$), which is due to the spindle knots-guided growth. The mechanical strength of air filter is positively correlated with the NF diameter [30,31]. In Fig. 1c, d, the diameters of the HNM-NFs were larger than that of the pure PCL NF with the incorporated spindle knots, corresponding to higher values for elasticity modulus and strain peak stress of the HNM-NF filter. However, the mean diameter was smaller for HNM-NFs with HNM ratio of 11 wt% ($0.74 \pm 0.22 \mu\text{m}$), which may be related to the overlarge spindle knots due to HNM aggregation. The fiber diameter is positively correlated with the solution viscosity under the constant electrical potential, and the solution viscosity is dependent on the HNM mass ratio [14]. The overlarge spindle knots caused additional gravity stretching, leading to fiber elongation and diameter shrinkage.

In Fig. 1e, the strips of the HNM-NF filter (2 cm $\times$ 10 cm) easily exhibited different extents of *in situ* twisting (0°, 90°, 180° and 360°) with spiral shape, indicating excellent pliability and flexibility [32]. PM_{2.5} filtration performance test was performed with the filters containing different concentrations of HNMs under various humidity levels (Fig. S2) [1,3]. The schematic of the pressure drop measurement is shown in Fig. 1f. By increasing the relative humidity (Fig. 1g), the η of the HNM-NF filters increased. On the contrary, for the PCL (0 wt%) and HNM-NF filters of 11 wt%, η decreased when the humidity increased from 30% to 40%. The efficiency improvement was attributed to the increased PM_{2.5} particle viscosity and intensified interactions between particles and the HNM-NF filters as the humidity increased [26,33,34].

For the filtration performance, the removal efficiency of PM_{2.5} was the highest for the HNM mass ratio of 7 wt%, which was $88.10\% \pm 0.56\%$, $89.27\% \pm 0.32\%$ and $90.46\% \pm 0.48\%$ at 30%, 40% and 50% humidity, respectively. Simultaneously, the quality factor was also the highest, which was 1.4 times that of the control (Table S1), indicating the best filtration ability. The PM_{2.5} particle removal efficiency of HNM-NF filter was improved by ~14% compared with the PCL filter (76% vs. 90%). It indicates that the spindle-knot-like HNM-NFs could significantly enhance the PM_{2.5} filtration performance. Furthermore, the as-prepared HNM-NF filter exhibited a 90.46% PM_{2.5} removal efficiency at an ultralow pressure drop (39 Pa) [1,25], varied from the other previously reported filters in η (~99%) and pressure drop (>110 Pa) (Table S2) [35–37]. HNM-NF (0.23 ms^{-1} , ~39 Pa) showed obvious low pressure drop than that of products

(0.35 ms^{-1} , $>63 \text{ Pa}$; 0.21 ms^{-1} , 206 Pa ; 0.06 ms^{-1} , 112 Pa) in literatures. More importantly, the HNM-NF filters with a thickness of $74 \mu\text{m}$ show a higher filtration effect ($>85\%$) than the pure PCL filter (76%). It is worth noting that the spinning thickness of the experimental equipment is not as good as that of industrial production equipment, while it is a key factor affecting the η and air resistance [1,38].

Filtration stability and wettability of HNM-NF filter

To investigate the stability of the filtration [3], the evo-

lution of the filtration performance of the HNM-NF filters was evaluated for 3600 s (Fig. 2a). The NF filters with different mass ratios of HNM showed a stable filtration effect over a period of time. The filtration effect maintained stable at $76.69\% \pm 1.22\%$ for electrospun PCL NF filter, and it was increased to $80.74\% \pm 1.04\%$, $86.71\% \pm 0.91\%$, $86.24\% \pm 1.92\%$ and $85.22\% \pm 1.33\%$ for the 5, 7, 9 and 11 wt% HNM-NF filters, respectively. The HNM-NF filters with a thickness of $74 \mu\text{m}$ show a higher and more stable filtration effect ($>85\%$) than the pure PCL filter (76%) within 3600 s. Furthermore, the variation of the η

Figure 2 The filtration stability, air penetration, polarity and wettability of HNM-NF filters. (a) $\text{PM}_{2.5}$ removal efficiencies of 0, 5, 7, 9 and 11 wt% HNM-NF filters for a period time (3600 s). Left, magnified view for the first 80 s. (b) The pressure drops, porosities, (c) spindle-knot morphologies on a single fiber. Insets: static contact angles of 0, 5, 7, 9 and 11 wt% HNM-NF filters. Scale bars, $2 \mu\text{m}$. (d) Schematics showing the mechanism of high surface energy on HNM-NF filter. (I) Joint angles between spindle-knot and NF; (II) the polar surface induced by polar groups of HNMs (scale bar, $5 \mu\text{m}$); (III) the relationship between surface roughness and surface energy on HNM-NF filters. (e) The dynamic contact angle evolution of a water droplet falling on 0, 5, 7, 9 and 11 wt% HNM-NF filters.

for the first 80 s was displayed in the left of Fig. 2a, and the 0, 5, 7, 9 and 11 wt% HNM-NF filters reached a stable value in 58, 44, 54, 45, and 56 s, respectively. The HNM-NF filters achieved more rapid and steady capture of PM_{2.5} than the PCL filter (0 wt%). Traditionally, the air filter would be replaced periodically or when the dust capacity reaches saturation, which cannot be or is very difficult to reuse [5].

The pressure drop test was performed to quantitatively analyze the air penetration, which was an important parameter for filtration performance [34]. The pressure drops at a face velocity of 0.23 ms⁻¹ were only 39.57, 39.41, 39.05, 39.00 and 39.00 Pa for the 0, 5, 7, 9 and 11 wt% HNM-NF filters, respectively (Fig. 2b). Importantly, the pressure drop of HNM-NF filter (0.23 ms⁻¹, ~39 Pa) showed an obvious decrease compared with the N95 facemask (0.30–0.40 ms⁻¹, 350 Pa) under a same face velocity level [39], indicating the robust air penetration characteristics of the spindle-knot-like structures. Hence, combined with the previous results (Table S2), HNM-NF filters exhibited superior performance as air filters at an ultralow pressure drop.

Further, the HNM-NFs also possessed high porosity, amazing mono-fiber morphology and surface wettability. The porosity (1- α) could be expressed by the equation [14] in Fig. 2b, which were 0.956, 0.947, 0.916, 0.931 and 0.929 for the 0, 5, 7, 9 and 11 wt% HNM-NF filters, respectively. The porosity was minimal for the 7 wt% HNM-NF filter. The decreased pore size of electrospun NFs may result from the spindle-knot structure [25]. The morphology of the spindle knots of the mono-fiber was presented (Fig. 2c). The surface of the spindle knots was wrinkled due to the wrapped HNMs. The joint angles of the spindle knot and NF, which were related to the hydrophilicity, were 180°, 152.6°, 139.9° (minimum), 149.6° and 153° for the 0, 5, 7, 9 and 11 wt% HNM-NF filters, respectively. In the insets of Fig. 2c, the static contact angle of the 7 wt% HNM-NF filter was also the smallest among the filters (0 wt% (128°), 5 wt% (117°), 7 wt% (112°), 9 wt% (121°) and 11 wt% (122°) HNM-NF filters), indicating an improvement of hydrophilicity [40]. HNM-NF filter showed higher hydrophilicity compared with the pure PCL filter due to incorporated HNMs. Further more, PM capture performance could be enhanced by HNMs spindle knots for its structure and hydrophilicity, especially in high humidity environment.

In Fig. 2d, combined with the results of fiber diameter analysis, the schematic layout illustrated that: (i) a smaller joint angle for the junction between the spindle knots and NFs resulted in more bulges in the spindle knots and

further smaller pore spaces between NFs [25]. (ii) In HNTs, there were different chemical constituents. The Si-O-Si groups on the external surface and Al-OH groups on the internal surface determined the negatively charged outer surface of the HNMs, resulting in an increase in the spindle-knot surface polarity [28,41]. (iii) The surface energy of the NFs was well fitted with Wenzel's law:

$$\cos\theta_w = r\cos\theta, \quad (1)$$

where r , θ and θ_w are the surface roughness, the intrinsic contact angle of the smooth surface and the apparent contact angle of the rough surface, respectively [27]. The schematic layout illustrated that the surface of the spindle knots was rougher than that of the fiber, resulting in higher surface energy and greater hydrophilicity. Droplet jumping on the surfaces of the HNM-NF filters was applied to investigate the dynamic wetting behaviour (Fig. 2e). Droplet jumping on the 7 wt% HNM-NF filter reached static status more quickly (700 ms) than the 0 wt% (1052 ms), 5 wt% (1008 ms), 9 wt% (780 ms) and 11 wt% (944 ms) HNM-NF filters. This difference was attributed to its more hydrophilic surface, leading to stronger adhesion to a water droplet, and thus the droplet would stop moving more rapidly [40]. Therefore, constructing spindle knots can increase the surface energy and hydrophilicity to ensure stable PM_{2.5} η .

The mechanism of PM capture

The excellent PM capture performance of HNM-NF filter was mainly attributed to the pore structures created by the spindle knots on the filters. The pore properties and the PM capture mechanism were studied and illustrated in this part. The surface area analyzed with BET (Fig. S3a) showed a sharp capillary condensation step in the N₂ adsorption-desorption isotherms of the 0 wt% HNM-NF filter at high relative pressures ($P/P_0=0.90-0.99$), indicating a relatively large pore size. The isotherm of the 7 wt% HNM-NF filter showed a gentler capillary condensation step, indicating a relatively small pore size [42–44]. All the isotherms of the HNM-NF filters were type IV with H₃-type hysteresis (the inset in Fig. S3a), which was characteristic of mesoporous structure [31].

In the HNM-NF filters, a higher adsorption volume, slower desorption process and broader desorption branch indicated the increase of mesopores induced by the spindle knots [31]. The pore volume of HNM-NF filters was larger than that of pure PCL filter, as shown in Table S3. The PCL (0 wt%) NF filter exhibited a unimodal size distribution of pores within the range from 12 to

Figure 3 The mechanism of PM capture for HNM-NF filters. (a) The schematic of the spindle-knot structures on HNM-NF filters. (I) Top view and (II) sectional view of HNM-NF filters with and without spindle knots, respectively. (I, II) Left: the schematics of the structural differences on the 2D surface and 3D hierarchy; right, the SEM images of HNM-NF filters. Scale bars: (I), 20 μm ; (II), 50 μm . (b) The PM_{2.5} removal efficiencies, pressure drops and (c) quality factors of 0 and 7 wt% HNM-NF filters for 24-h road dust test. (d) The top surface morphologies of 0 and 7 wt% HNM-NF filters for 24-h road dust test. Scale bars, 2 μm . (e) Schematic illustrations of the PM_{2.5} filtration process: (I, II) the filtration processes of HNM-NF filters with and without spindle knots, respectively. The insets in (I, II) were the magnified schematics.

16 nm. The pore size distributions for the 5, 7, 9 and 11 wt% HNM-NF filters were broader, which could be

categorized into two hierarchy levels. For the small pores, the distribution center was shifted to the left (Peak 2

appeared at the left of Peak 1, 8–16 nm), while the large pore distribution was concentrated at 18–30 nm (Peak 3). In Fig. S3b, the pore size curves of HNM-NF filters showed shrinking pore size on 2D surface with a bimodal distribution, while the pure PCL filter showed large pore size with a unimodal distribution. The increased pore volume and shrinking pore size were beneficial to the dust holding capacity and PM filtration in reality.

The shrinking pore size formed in 2D pattern and the fluffy 3D reticular architecture were attributed to the complicated weaving and stacking modes of both spindle knots and NFs. An ideal model was the simplification of substantive filter structure with efforts to better represent both 2D and 3D patterns. The decreased size of pores shown on a 2D surface (schematic in Fig. 3aI) shared a similar result with the SEM images [25]. The large pore volume was attributed to the increased distance between NF layers on a 3D reticular architecture (schematic in Fig. 3aII) [8]. In the cross-section SEM images (under the same electrospinning conditions), the thickness of the PCL filter was 62.59 μm , while the thickness of the 7 wt% HNM-NF filter increased to 74.17 μm . The increase in thickness was also consistent with the increase in the pore volume and surface area of the HNM-NF filters (Table S3). It is worth mentioning that the high pore volume (7 wt% HNM-NF, 0.009837 $\text{cm}^3 \text{g}^{-1}$) is beneficial to the dust holding capacity of the HNM-NF filters, which is a vital parameter for air filtration [16]. The spindle knot is the key to enhance the $\text{PM}_{2.5}$ capture under high air permeability, more effectively in several monolayers [8].

The pressure drops and PM removal efficiencies under continuous 24-h road dust test of the representative 0 and 7 wt% HNM-NF filters were investigated, as shown in Fig. 3b and Fig. S3c, d. With a persistent high PM removal efficiency (0 wt%: >74.0%; 7 wt%: >85.0%), the pressure drops of both 0 and 7 wt% HNM-NF filters are stable and show a small fluctuation range between 39.0 and 40.3 Pa. After 24-h PM filtration test, the pressure drop of PCL filter (0 wt%) increases from 39.1 to 39.3 Pa, while the pressure drop of 7 wt% HNM-NF filter increases from 39.0 to 40.3 Pa. The slightly increased pressure drop is attributed to more $\text{PM}_{2.5}$ particles captured on the HNM-NF filter, indicating a higher PM removal efficiency. The pressure drop of HNM-NF filter (0.23 ms^{-1} , ~40.3 Pa) still showed an excellent permeability to airflow compared with the N95 facemask (0.30–0.40 ms^{-1} , 350 Pa) under the same face velocity level [39].

The quality factor (Q_f) is a key criterion to evaluate the comprehensive filtration performance of air filters. The Q_f

could be calculated by the equation in Fig. 3c, where ΔP is the pressure drop [23]. As presented in Fig. 3c and Table S4, the quality factors keep a stable trend throughout 24-h filtration test. The initial quality factor of 7 wt% HNM-NF filters (0.09819) is almost twice that of PCL filters (0 wt%, 0.05045). Importantly, the quality factor of 7 wt% HNM-NF filters (0.06701) is obvious higher, which is still 1.5 times that of PCL filters (0.04509) after 24-h PM filtration test. The sustained and stable high quality factor confirmed the high comprehensive filtration performance of HNM-NF filters (including the stability and reusability), indicating the superiority of spindle-knot structures on air filter for PM filtration.

The morphologies of PCL and 7 wt% HNM-NF filters after 24-h road dust test were observed by SEM. After 24 h, on top surface, the amount of $\text{PM}_{2.5}$ particles adhering on the HNM-NF filter was much more than that on the PCL filter (Fig. 3d); while on the bottom surface, there was no particle adhering on the PCL filter but a few particles was observed on the HNM-NF filter (Fig. S3e). This difference was ascribed to two reasons: (i) most of $\text{PM}_{2.5}$ particles were collected on the top surface of the filter and rarely penetrated to the bottom surface [8]; (ii) the $\text{PM}_{2.5}$ particles that penetrated to the bottom surface can be carried away by the airflow on the PCL filter, whereas those particles can be firmly captured on the HNM-NF filter due to the polarized surface and hydrophilicity, resulting in a good filtration performance [32]. Furthermore, HNM-NF filters showed the possibilities for better PM capture capacity because PM was only adsorbed on fibers and no aggregation of bigger particles after 24-h road dust test [1].

HNM-NF filter structure and its hydrophilicity were improved by the bio-inspired design of spindle knots, which were beneficial to the filtration performance and met the low pressure drop requirements especially in humid environment [23]. Based on above results, a particle filter model for HNM-NF filters was proposed and illustrated (Fig. 3e), as following: (i) $\text{PM}_{2.5}$ could easily pass through the PCL filter because of the large pore size; (ii) after constructing the spindle-knot structures on the NFs, $\text{PM}_{2.5}$ could be effectively purified with the HNM-NF filter.

This difference was related to the characteristics of the HNM-NF filters. The electrospun NF as the main part of air filter acted as not only a support material but also partial PM filtration blocking. While the pure PCL NF as air filter was undesired with a low PM removal efficiency, which could not effectively capture the $\text{PM}_{2.5}$ on the filter, as shown in Fig. 3d. The HNMs spindle knots fa-

cilitate a higher surface energy and hydrophilicity for the whole HNM-NF filter surfaces [27,28], as shown in Fig. 2d, e. Thus, compared with pure filter, the PM particles could be effectively captured and adsorbed on the whole HNM-NF filter surfaces (including both the fiber and spindle knot), which was consistent with experimental phenomenon (Fig. 3d, e). The size of the pores between NFs was effectively decreased on the 2D surface, increasing the capture potential for PM_{2.5} particles. The striking enlarged pore volume on the fluffy 3D reticular architecture can also improve the dust holding capacity.

Thus, the spindle-knot structures on the HNM-NF filters can realize a stable and effective air filtration performance.

Structure, chemical composition and assembly of HNM-NF filters

The structure and chemical composition of the HNM-NF filters were investigated to further determine the properties of the filters. The effects of HNMs incorporation on the filter composition were further evaluated with FTIR spectra (Fig. S4a). The characteristic peaks of PCL, asymmetric C–O–C stretching, C–C and C–O stretching, C=O stretching, symmetric CH₂ stretching and asymmetric CH₂ stretching appeared at 1240, 1294, 1729, 2867

and 2949 cm⁻¹, respectively. A minor change in the characteristic peak (962 cm⁻¹, O–H stretching) was observed after the incorporation of HNMs, indicating no significant composition changes on the fibers of the PCL matrix [45]. The XRD patterns indicated that the crystal structure of the HNMs was transformed into amorphous silica after calcination at 550°C (Fig. S4b, c). The result was consistent with the FTIR analyses. The characteristic diffraction peaks of PCL NFs were located at 16.3°, 21.4° and 23.6° (the right of Fig. S4b). The weak diffraction peak at 22.5° appeared after the incorporation of HNMs, illustrating that the HNMs were incorporated into the PCL NF matrix [45]. The HNMs with polar functional groups showed strong dipole interactions with PM_{2.5} particles, thus improving η .

The structure and composition of the spindle knots in the HNM-NF filters were further investigated *via* TEM [17,45]. In Fig. S4d, the surface of the spindle knots on the HNM-NFs was rough and wrinkled after wrapping some matters, but the other part of the surface on the HNM-NF was smooth and even. In the relevant EDX mapping analyses, the fibers and outer layer of the spindle knots were composed of C and O (the top of Fig. 4a), whereas the inner center of the spindle knots was composed of Al, Si and O (the bottom of Fig. 4a). The EDX elemental analysis revealed the same results (Fig. S4e),

Figure 4 The structure, chemical composition analyses and assembly evolution of HNM-NF filters. (a) EDX elemental mapping analyses of Si, Al, O and C for the single fibers of HNM-NFs (top, 0 wt%; bottom, 7 wt%). Scale bars: 1 μm. (b) The cross-section images of the PCL fiber and spindle knot on HNM-NF filter by FIB analyses. (c) Schematic illustrations showing the differences in various assembly layers between 0 and 7 wt% HNM-NF filters. (I, II) Sectional view and top view, respectively.

indicating that the spindle-knot architecture was successfully constructed with the HNMs [18].

Furthermore, cross-section images of the PCL fiber and spindle knots were acquired with FIB (Fig. 4b) by sputtering a trench normal to the surface of the spindle knots [46]. An obvious dividing line can be observed between the inner center and the outer layer of the spindle knot. However, the PCL NF showed a uniform composition without the dividing line, indicating that the spindle knots were constructed by HNMs wrapped in PCL fibers. This result was consistent with the TEM results and the EDX analyses, indicating that the spindle-knot structures were derived from HNMs instead of the structural irregularity induced by HNTs agglomeration [31]. Through Rhino software simulation (Fig. 4c), a schematic was developed to illustrate the difference in the assembly of one, three and five layers of the HNM-NF filters with or without spindle knots. The spindle-knot architecture

created denser surfaces and richer interlayer structures in the filters, ensuring excellent air filtration performance [8].

Functional application and volume production of spindle-knot filters

PM_{2.5} collection capacity of the spindle-knot structure was confirmed by experimental results and theoretical mechanism. The spindle-knot structure fabricated with other nanomaterial microspheres was designed and incorporated in NFs. Al₂O₃, ZnO and TiO₂ NPs were chosen to construct microspheres through spray drying [17,47,48], as shown in Fig. S5a. Then, the Al₂O₃, ZnO and TiO₂ microspheres were used to construct spindle knots on NFs by electrospinning (mass ratio: 7 wt%). The morphology of the filters was characterized (Fig. 5a). All three types of microspheres succeeded in constructing the spindle knots, which were evenly distributed in the NFs,

Figure 5 Functional application, large-scale production and commercial filter cartridge fabrication of spindle-knot filters. (a) SEM images of electrospun filters containing 7 wt% Al₂O₃, ZnO, TiO₂ and HNMs microspheres, respectively. Scale bars: 20 μ m. The insets are the corresponding high-magnification images of the single spindle knots. Scale bars of the insets: 2 μ m. (b) The cross-section images of the Al₂O₃, ZnO, TiO₂ and HNMs spindle knots by FIB analyses. Scale bars: 500 nm. (c) The PM_{2.5} and PM_{10-2.5} removal efficiencies of Al₂O₃, ZnO, TiO₂ microsphere filters and PCL filter, respectively. (d) Schematic illustrations of the volume production process of HNM-NF filter. (I) The photograph of a large-scale HNM-NF filter prepared by the electrospinning process. The insets were the substrate, the prepared filter and the schematic of spindle-knot structures on the filter. (II) The prepared HNM-NF filter cartridges.

consistent with the HNM-NF filters. It demonstrated that the construction of spindle knots on NFs by electrospinning was a facile and universal method.

Furthermore, to explore the spindle-knot structures of Al_2O_3 -NFs, ZnO -NFs and TiO_2 -NFs, XRD, EDX and FIB analyses were performed. In the XRD patterns, the weak characteristic diffraction peak of Al_2O_3 appeared for the Al_2O_3 -NFs, evidencing that the Al_2O_3 microspheres were embedded in the PCL NF matrix (Fig. S5b). In the EDX analyses (Fig. S6), the center of the spindle knots on the Al_2O_3 -NF filter showed high Al content distinct from other parts of the NFs, indicating a strong association between spindle knots and Al_2O_3 microspheres. In the FIB analysis, the Al_2O_3 -NF spindle knot was examined: the inner center was a microsphere with a dividing line apart from the outer layer (Fig. 5b), demonstrating that the spindle-knot structure was constructed by trapping microspheres in the PCL NFs. The ZnO -NF and TiO_2 -NF filters exhibited similar results as the Al_2O_3 -NF filter. In short, there were various materials available for constructing spindle knots [17,46].

The Al_2O_3 -NF, ZnO -NF and TiO_2 -NF filters showed good filtration performance for $\text{PM}_{2.5}$ and PM_{10} particles, with the $\text{PM}_{2.5}$ removal efficiencies of $79.14\% \pm 0.60\%$, $80.06\% \pm 0.64\%$ and $76.56\% \pm 0.54\%$, and PM_{10} removal efficiencies of $79.80\% \pm 0.76\%$, $80.89\% \pm 0.61\%$ and $77.21\% \pm 1.15\%$ (Fig. 5c), respectively. Compared with the PCL filter ($\text{PM}_{2.5}$: $74.08\% \pm 0.54\%$; PM_{10} : $75.02\% \pm 1.06\%$), all the three filters showed obvious improvements on $\text{PM}_{2.5}$ and PM_{10} capture efficiencies, although inferior to those of the HNM-NF filters. The difference was ascribed to the difference in the polarity of the spindle-knot materials. Fig. 5d shows photographs of the large-scale production of HNM-NF filter with the length of 15 m and width of 0.66 m (the minimal industrial production standard referred to the electrospinning equipment MF01-001). It could be processed by ultrasonic composite, folding, framing and forming to produce a filter cartridge [38]. The magnified images in Fig. 5dI illustrates the spindle-knot structures on the large-scale filter, and the prepared filter cartridge could be applied in an air purifier (Fig. 5dII), demonstrating the great potential of this method in practical applications.

CONCLUSIONS

In summary, a bio-inspired spindle-knot NF filter was constructed by HNM fabrication *via* a spray-drying process and spider-silk-shaped NF formation with the electrospinning process. The outer shrinking pore size formed by NFs weaving in 2D pattern enhances the $\text{PM}_{2.5}$

capture capacity, the inner fluffy 3D reticular architecture with spindle knots and thus increased distance between NF layers promotes the dust holding capacity, and a hydrophilic surface and higher surface energy can further enhance $\text{PM}_{2.5}$ particle adhesion, even supporting the future applications of spindle-knot NF filters in biological protection materials for high-risk outbreak prevention and control. The biocompatible polymer, such as poly(lactide-co-glycolide), polyvinyl alcohol and poly-tetrafluoroethylene, could be processed into spindle-knot-like NFs to meet the strict requirements for haemostasis dressing. Therefore, we believe that the spindle-knot NF filter plays an important role in specific environment protection, and the desired shape structures could be used for tissue engineering, biological protection and smart wearable devices.

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Author contributions Zhang Y, Ouyang J and Yang H conceived the concept; Huang Z and Liao J prepared and characterized the materials; Huang Z, Zhang Y and Yuan F analyzed the data and wrote the manuscript, which was reviewed and revised by all authors. All authors read and approved the final manuscript.

Conflict of interest The authors declare that they have no conflict of interest.

Supplementary information Experimental details and supporting data are available in the online version of this paper.

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纺锤状纤维结构的设计及其PM_{2.5}过滤性能研究

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摘要 城市雾霾, 特别是其中的PM_{2.5}颗粒(当量直径 $\leq 2.5\ \mu\text{m}$), 因其自身危害及其携带的病原体对公共健康具有严重威胁而被人们广泛关注. 静电纺丝纳米纤维作为空气过滤膜实现PM_{2.5}高效捕获是国内外研究热点, 但现有的纺丝滤膜仍存在无法兼顾高过滤效率和低空气阻力的问题. 根据蛛丝微观结构特点, 采用静电纺丝技术, 通过在纺丝纤维内部引入不同形貌黏土矿物及其微球前驱体的策略, 可实现复合纤维及其滤膜材料的多级结构构筑和微观形貌调控, 成功设计具有纺锤状埃洛石微球节点的仿生纳米纤维滤膜材料. 其纤维表面富含亲水基团及活性位点, 粗糙的表面形貌具有高表面能及PM_{2.5}颗粒的强捕获性. 对比纯纺丝滤膜($62.59\ \mu\text{m}$), 纺锤状节点滤膜具有蓬松的纤维膜层间架构($74.17\ \mu\text{m}$)及窄尺寸的表面孔隙, 可实现稳定高效的PM_{2.5}过滤效率($>85.0\%$)及持续低压差阻力($\sim 39\ \text{Pa}$). 本文探索了纳米纤维的官能化、多层次结构构建和微观形貌调控对纺丝滤膜过滤性能的影响及其过滤机制理论, 为其他新型高性能高分子纳米纤维复合材料的设计和开发提供了借鉴.