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**Mussel-inspired approach to cross-linked functional 3D nanofibrous aerogels for
energy-efficient filtration of ultrafine airborne particles**

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ABSTRACT

Polymer aerogels fabricated using conventional methods typically have relatively narrow mono-modal pore size distribution (PSD), and relatively thick and tight pore walls. Herein, inspired by mussel glue, cross-linked three-dimensional (3D) polyacrylonitrile (PAN) nanofibrous aerogels (NFAs) with ultrahigh porosity, hierarchical porous structures, and good compression resistance are successfully fabricated via electrospinning, facile polydopamine (PDA) coating and crosslinking by ferric ions (Fe^{3+}) followed by freeze-drying. Morphology characterization and compression tests show that both multiple hydrogen bonding facilitated by the PDA coating and Fe^{3+} -PDA coordination bonding could effectively induce the formation of inter-fiber junctions, enhancing compression resistance of the 3D NFAs and leading to hierarchical porous structures with a very wide PSD. When a thin layer of the optimized 3D NFA with a large specific surface area ($85.7 \text{ m}^2 \text{ g}^{-1}$) is combined with a commercial air filter, the composite filter obtained exhibits high filtration efficiencies of 99.72% and 99.85% for airborne particles with sizes of $< 100 \text{ nm}$ and $< 500 \text{ nm}$, respectively, at a low pressure drop of only 54.1 Pa. The results show that the cross-linked NFAs could act as a highly efficient air filter for ultrafine particles while not increasing the overall pressure-drop significantly, which are due to the good adhesive properties of PDA, electrostatic charge induced by Fe^{3+} , and high porosity and hierarchical porous structures of the 3D NFAs.

Keywords: *aerogel, electrospinning, polydopamine, air filtration, particulate matter*

1. Introduction

Aerogels are three-dimensional (3D) porous materials, which typically exhibit ultrahigh porosity ($> 99\%$), ultralow density, large specific surface area and low thermal conductivity because voids take up 99% volume.¹ With these unique features, aerogels are widely used for a wide variety of applications such as catalysis supporter, thermal and acoustic insulation, air and water purification, gas separation, energy storage and sensors.²⁻⁴ Aerogels can be divided into polymer aerogels,⁵⁻⁸ carbon-based aerogels,⁹⁻¹⁰ and biomass-based aerogels^{6, 11}. Among them, polymer aerogels have drawn great attention due to their diverse chemical structures, good environmental stability and mechanical properties. Conventional methods for the preparation for polymer aerogels involve gelation (sol-gel transition), aging (network perfection) and drying (gel-aerogel transition).¹² All these three steps affect the structures and properties of polymer aerogels, of which drying is essential for preserving the network structures of the wet gels. There are two common drying methods, supercritical drying and freeze drying; the former yields nanopores of several to tens of nanometers, while the latter gives much larger pores of 1-100 μm . Therefore, there is a need to develop a new process for fabrication of polymer aerogels that exhibit not only ultrahigh porosity but also controllable hierarchical and open porous structures with wide pore size distribution (from nanometers to micrometers), as well as good mechanical properties for desired application fields.

Highly porous 3D polymer nanofibrous aerogels (NFAs) with nanofibers as the building blocks have attracted much attention in recent years, especially in air filtration field as the ultrahigh porosity of the NFAs can provide longer residence time to ultrafine particles that undergo Brownian motion, thereby having the potential to achieve high filtration efficiency for ultrafine particles.^{6, 13} Besides, the increase of filtration efficiency would only be accompanied by a small increase in pressure drop owing to the ultralow packing density and unique airflow regime of the 3D filters. Moreover, slip flow of air molecules on the periphery of nanofibers becomes significant when the fiber diameter decreases to $< 500\text{ nm}$,¹⁴⁻¹⁵ which also helps to reduce the pressure drop.

3D NFAs have been fabricated using various methods,¹⁶ such as multi-layer electrospinning,¹⁷ folding or stacking two-dimensional (2D) nanofiber membranes,¹⁸⁻¹⁹ template/liquid-assisted collection followed by removing template or freeze-drying,²⁰⁻²¹ and self-assembly of electrospun nanofibers^{4, 6, 22}. The poor structural stabilities of these highly porous 3D polymeric NFAs, however, make them unsuitable for air filtration applications as airflow-induced compression force may cause the highly porous NFAs collapse to much denser ones.

To make the 3D NFAs more robust, a straightforward strategy is to create inter-fiber junctions. In this work, we used a mussel-inspired approach to simultaneously cross-link and surface-modify polymer nanofibers to form mechanically robust 3D NFAs with versatile adhesive surface. Briefly, electrospun polyacrylonitrile (PAN) nanofibers suspended in a basic aqueous solution could be facially coated with a thin layer of polydopamine (PDA), a polymeric mimic of mussel adhesive protein. Like mussel glue, PDA is rich in catechol groups that are capable of forming coordination bonds with transition metal ions, such as Fe^{3+} .²³⁻²⁶ Thus, by treatment of PDA-coated PAN nanofibers (PDA@PAN) with a solution of ferric ions, inter-fiber junctions could form in subsequent freeze-drying process via the formation of inter-fiber Fe^{3+} -catechol coordination bonds, leading to cross-linked aerogels (Fe^{3+} -PDA@PAN). The cross-linking not only boost the mechanical properties of the NFAs, but also lead to hierarchical pore structures that can be easily controlled by adjusting Fe^{3+} concentration in the treatment. Moreover, the catechol groups could interact with various chemicals through noncovalent interactions including hydrogen bonding, π -stacking and charge transfer.²⁷ Thus they may help bind pollutant particles efficiently. Fe^{3+} ions may also offer electrostatic interaction, facilitating the adsorption of negatively charged pollutant particles.²⁸ Herein we demonstrate that the cross-linked 3D NFAs fabricated using our approach indeed exhibits high porosity and enhanced compression resistance. When such a NFA is combined a commercial high-efficiency particulate arrestance (HEPA) air filter, the hybrid filter exhibits enhanced filtration efficiency for ultrafine particles with only a slight increase in pressure drop. This mussel-inspired approach also

provides a new generic route for fabrication of robust functional NAFs for various applications.

2. Materials and methods

2.1. Materials

Polyacrylonitrile (PAN, Mw=150 000), iron (iii) chloride hexahydrate, dopamine hydrochloride (DA, 98%), tris(hydroxymethyl)aminomethane (Tris, 99%), N, N-dimethylformamide (DMF), and tert-butanol were purchased from Sigma-Aldrich (USA) and used as received. All reagents were of analytical grade and used without further purification. Deionized (DI) water was used as the solvent throughout the experiments. Commercialized HEPA filters were purchased from Liaoning Mingchuang Environmental Protection Technology co. LTD, China.

2.2. Preparation of electrospun nanofibrous 2D mats and 3D aerogels

PAN nanofibers were prepared by electrospinning a PAN solution (9.0 wt% PAN in DMF) at 40% RH humidity. The flow rate, voltage applied to the needle tip and working distance were set at 0.5 mL h⁻¹, 10 kV and 15 cm, respectively. For fabrication of 3D nanofibrous aerogels (NFAs), a piece of steel wire mesh (5 mm diameter) immersed in a mixture of tert-butanol and water (weight ratio = 1:1) was used to collect the nanofibers. The as-spun PAN nanofibers were then transferred together with the wire mesh into a freshly prepared aqueous solution of DA (0.25 mg mL⁻¹ in Tris buffer, PH=8.5) for coating of PDA at room temperature for 4 h. After the reaction, the PDA-coated PAN nanofibers, denoted as PDA@PAN nanofibers, were purged with DI water for several times. To cross-link PDA@PAN nanofibers via PDA-Fe³⁺ complexation, they were immersed in FeCl₃ solutions of various concentrations (0.025 mg mL⁻¹, 0.25 mg mL⁻¹ and 2.5 mg mL⁻¹) respectively. Finally, after purging with DI water, PDA@PAN and Fe³⁺-treated PDA@PAN (Fe³⁺-PDA@PAN) nanofibers with wire mesh were frozen in a refrigerator and then freeze-dried to obtain thin 3D NFAs supported on wire mesh. Thin PAN NFA was obtained by directly freeze-drying PAN nanofibers with wire mesh in tert-butanol and water. Thick PAN, PDA@PAN and Fe³⁺-

PDA@PAN NFAs with dimensions of about 20 mm in diameter and 12 mm in height were also prepared using the same procedure without the wire mesh for mechanical testing. In this work, Fe³⁺-PDA@PAN samples obtained by the treatment with FeCl₃ solutions of concentrations of 0.025 mg mL⁻¹, 0.25 mg mL⁻¹ and 2.5 mg mL⁻¹ were marked as Fe³⁺-PDA@PAN-0.025, Fe³⁺-PDA@PAN, and Fe³⁺-PDA@PAN-2.5 respectively. PAN, PDA@PAN and Fe³⁺-PDA@PAN 2D nanofibrous mats were prepared using a similar procedure except that the collector is the wire mesh standing on aluminum foil.

2.3. Characterization

The structures and morphologies of the as-prepared samples were investigated by a field emission scanning electron microscopy (FESEM, JEOL JSM 7600) at an acceleration voltage of 5 kV. The densities of the NFAs were estimated by measuring the weights and dimensions of the cylindrical-shaped NFAs. Three samples were measured to obtain the average value. Porosity of the NFA is defined as the volume fraction of void, *i.e.*, $\text{Porosity} = 1 - \rho_{\text{NFA}} / \rho_{\text{polymer}}$, as ρ_{Aerogel} means the measured density of the aerogel, while ρ_{polymer} means theoretical density of the solid polymer. The specific surface area and pore size distribution were characterized by a surface area and porosity test instrument (Micromeritics, Tristar II 3020) by N₂ physisorption at 77 K. A tensile tester Instron 5567 with a 10 N load cell was used to perform compression tests on the thick NFAs at the compression rate was 1.0 mm min⁻¹. Cyclic compression mechanical properties of the NFAs were also tested at the compression strain of 5% for 100 cycles. Contact angle measurements were conducted using contact angle dataphysics (OCA 15Pro) with DI water and diiodomethane (CH₂I₂) as the probe liquids. X-ray photoelectron spectroscopy (XPS) measurements were collected on a device of Kratos Analytical AXIS with a monochromatized Al Ka X-ray source (1486.6 eV photons). All XPS spectra were corrected using C1s line at 284.5 eV.

2.4. Air filtration test

For air filtration tests, model haze particles were generated by burning incense in an enclosed chamber. Clean air was used to dilute the incense smoke to a hazardous

pollution level equivalent to PM 2.5 (fine particulate matter with size of $\leq 2.5 \mu\text{m}$) concentrations between 400 and 500 $\mu\text{g m}^{-3}$. The particle concentrations before and after filtration were recorded using a combination of two particle counters: an optical particle sizer (TSI OPS 3330, TSI Instruments Ld), which could detect particles with sizes between 0.3 to 10 μm , and a condensation particle counter (TSI NanoScan SMPS 3910, TSI Instruments Ld), which could detect particles with sizes between 0.01 μm to 0.42 μm . The combined particle concentration data were tabulated using a normalization software (MIM, TSI Instruments Ld). Filtration efficiency (η) was calculated by comparing the particle weight concentration before and after filters. Pressure drop (Δp) across filters was measured using a differential pressure gauge (Digital Manometer, Bluewind Laboratory Pte Ltd). Quality factor (QF) defined by the formula: $QF = -\ln(1-\eta)/\Delta p$, was used to evaluate filtration capacity of the air filters based on their removal efficiency and air resistance. The wind velocity was measured by an air velocity meter (Airflow instruments velocity meter TA430, TSI Instruments Ltd). The face velocity used was 0.1 m s^{-1} at the humidity of 60% RH. The test system used in this work is shown in Fig. S1 and the test follows the international standards: GB/T 14295-1993, air filters, 2009-06-01; ANSI/ASHRAE standard 52.2-2012; method of testing general ventilation air-cleaning devices for removal efficiency by particle size.

3. Results and discussion

3.1. Structures and morphologies of Fe^{3+} -PDA@PAN 3D NFAs

The fabrication process for PAN-based 3D NFAs are illustrated in Fig. 1. The purpose of liquid collection is to create 3D loosely packing morphology of nanofibers to render high porosity to the resultant NFAs, providing large mean free path to ultrafine particles, while the cross-linking and freeze-drying steps help to fix such desired morphology into solid state and enhance compression resistance of the NFAs so that such morphology could be well maintained in the filtration process. In addition,

the catechol-rich and charged nature of the Fe^{3+} -PDA@PAN surface also facilitates adsorption of various types of particles.^{25, 29-31}

Fig. 1. Schematics showing the preparation processes of PDA@PAN and Fe^{3+} -PDA@PAN NFAs.

Morphologies of PAN, PDA@PAN and Fe^{3+} -PDA@PAN 3D NFAs are compared with that of PAN 2D nanofibrous mats in Fig. 2 and Fig. S2. From the SEM images, we could see that both 2D nanofibrous mats and 3D NFAs are composed of nanofibers with diameters of 200-300 nm. However, different from the PAN 2D mat (Fig. S2a), in which nanofibers are densely packed to form relatively flat, compact surface, in the PAN 3D NFA, the nanofibers form a much more porous morphology (Fig. 2a). At a higher magnification, many layers of nanofibers are clearly visible in the 2D mat (Fig. S2b), whereas only several nanofibers could be clearly observed in the top layer of the PAN 3D NFA and the nanofibers beneath look fuzzy (Fig. 2b) because their positions are much lower than the top layer. This further suggests the much higher porosity of the PAN 3D NFA.

After coating with PDA and treatment with ferric ions (unless specified, the concentration of the FeCl_3 solution used is 0.25 mg mL^{-1}), the highly porous morphology of 3D NFA is well retained (Fig. 2c and 2e). Moreover, partial merging of neighboring nanofibers occurs significantly in the Fe^{3+} -PDA@PAN NFA, as shown in circled regions in Fig. 2f, which is likely to be caused by inter-fiber Fe^{3+} -PDA complexation. Before the treatment by Fe^{3+} , no obvious bundling is observed in the PDA@PAN NFA (Fig. 2d). This partial bundling-induced cross-linking is beneficial to

compression resistance of the 3D NFAs. It also makes the NFAs more heterogeneous (Fig. 2e), and the resultant multiscale pore structure may help to reduce the resistance to airflow.³²⁻³³ The successful coating of PDA on PAN nanofibers is evident from the color change observed. The insets in Fig. 2a, 2c, 2e show that the PAN NFA is white, while after PDA is coated on the surface of PAN NFA, the NFA becomes yellowish. With the subsequent treatment with ferric ions, the color becomes slightly darker. This shows that PDA and Fe^{3+} have been successfully attached on the surface of PAN nanofibers.

Fig. 2. SEM images of PAN (a, b), PDA@PAN (c, d) and Fe^{3+} -PDA@PAN (e, f) 3D NFAs. The insets in a, c, e are the digital photographs of PAN, PDA@PAN and Fe^{3+} -PDA@PAN 3D NFAs with wire mesh as support.

To further verify the successful PDA coating and the coordination bonding between PDA@PAN nanofibers and Fe^{3+} , EDX (Fig. 3) and XPS (Fig. 4) studies were conducted. As shown in Fig. 3, EDX analysis of Fe^{3+} -PDA@PAN NFA shows the homogeneous distribution of O (from PDA) and Fe elements on the nanofibers. The atomic contents of C, N, O, and Fe are 63.1%, 27.8%, 7.7% and 1.4%, respectively (Fig. 3a). The atomic ratio of O/Fe is about 5.5, implying that a substantial amount of catechol groups on the PDA@PAN nanofibers form coordination bonds with Fe^{3+} .

Fig. 3. SEM (a) and EDX mapping images (b: O and c: Fe) of Fe^{3+} -PDA@PAN NFA.

The XPS full survey spectrum (Fig. 4a) confirms the presence of C, N, O and Fe elements. Based on the XPS data, the atomic ratios of C, N, O and Fe element in Fe^{3+} -PDA@PAN NFA are 70.57%, 16.67%, 10.54% and 2.21%, respectively. These are different from the EDX results because XPS gives the chemical composition in the near surface region, which is dominated by the PDA coating that has high C content and low N content. Nevertheless, the atomic ratio of O/Fe measured by XPS is still fairly high (4.8), confirming that a substantial amount of catechol groups on the PDA-coated nanofiber surface form coordination bonds with Fe^{3+} . As seen in Fig. 4b, the high-resolution C 1s spectrum of Fe^{3+} -PDA@PAN NFA exhibits three strong bands at 284.5 eV, 286.3 eV, and 287.9 eV, which can be assigned to Sp^2 C, C-O, and C=O, respectively. The C-O band can be safely assigned to catechol group, verifying the successful coating of PDA, whereas the presence of a small amount of C=O may be due to the oxidation of catechol groups by Fe(III). Indeed, the high-resolution of Fe 2p spectrum of Fe^{3+} -PDA@PAN NFA (Fig. 4c) exhibits relatively broad Fe $2p_{3/2}$ and Fe $2p_{1/2}$ bands. Each band could be deconvoluted into two components; the component with higher binding energies (712.8 eV and 726.4 eV) could be assigned to Fe(III) while the ones with lower binding energies (710.6 eV and 724.2 eV) could be assigned to Fe(II). By comparing these bands, we can see that Fe(III) is dominant in Fe^{3+} -PDA@PAN NFA, while a small amount of Fe(II) is present, which is produced by reduction of Fe(III). Besides, the peak deconvolution of N 1s spectrum of Fe^{3+} -PDA@PAN NFA (Fig. 4d) also exhibits three strong bands located at 399.4 eV, 400.5 eV, and 401.4 eV, respectively, which can be assigned to pyridinic-N (N-6), pyrrolic-N (N-5), and quaternary-N (N-Q). Both the bonding configurations of C and N element

show that Fe³⁺-PDA@PAN NFA has a highly polar surface, which will benefit haze particle adsorption.

Fig. 4. XPS survey spectrum (a), C 1s spectrum (b), Fe 2p spectrum (c), and N 1s spectrum (d) of Fe³⁺-PDA@PAN NFA.

To verify the multiscale pore structure observed in SEM studies (Figs. 2e,f), N₂ adsorption/desorption analysis was also conducted for Fe³⁺-PDA@PAN NFA. The specific Langmuir surface areas of Fe³⁺-PDA@PAN NFA is 85.7 m² g⁻¹, indicating that Fe³⁺-PDA@PAN NFA has large specific surface area. The isotherm curve of Fe³⁺-PDA@PAN NFA (Fig. 5a) belongs to type IV with a clear hysteresis loop, indicating that Fe³⁺-PDA@PAN NFA possesses a substantial amount of mesopores. The pore size distribution of Fe³⁺-PDA@PAN NFA calculated by the BJH method (Fig. 5b) is in the range of 15-1200 nm, and the center is about 425 nm, indicating that Fe³⁺-PDA@PAN NFA has hierarchical porous structures and a very broad size distribution. This would facilitate reducing pressure drop when the samples are used as air filters.

Fig. 5. Adsorption/desorption isotherms of Fe^{3+} -PDA@PAN NFA (a); the corresponding pore-size distribution of Fe^{3+} -PDA@PAN NFA as determined by the Barrett-Joynes-Halenda (BJH) method (b).

The data presented above indicates that Fe^{3+} treatment is effective in cross-linking the nanofibers in the NFAs and creating hierarchical porous structures. Furthermore, using this approach, the extent of cross-linking could be easily controlled by adjusting Fe^{3+} concentration used for the treatment.

Fig. 6. SEM images of Fe^{3+} -PDA@PAN NFAs obtained by ferric ion treatment at very low (0.025 mg mL^{-1} , a), middle (0.25 mg mL^{-1} , b), and high (2.5 mg mL^{-1} , c) Fe^{3+} concentration.

As shown in Fig. 6, the number of “inter-fiber junctions” in Fe^{3+} -PDA@PAN NFA could be increased significantly, by increasing the concentration of Fe^{3+} from 0.025 to 2.5 mg mL^{-1} . Comparing with the Fe^{3+} -PDA@PAN NFA obtained via the treatment at low Fe^{3+} concentration (Figs. 6a, 6b), bundling is much more extensive in the Fe^{3+} -PDA@PAN NFA obtained at high Fe^{3+} concentration (Fig. 6c). The extensive crosslinking would make the NFAs stronger, whereas it also leads to high packing density.

3.2. Density, porosity and compression resistance of the 3D NFAs

In order to study the effects of PDA coating and Fe^{3+} cross-linking on the compression mechanical properties of the 3D NFAs, cylindrical-shaped NFAs were prepared, and used as the compression test samples. Fig. 7 shows the typical stress-strain curves of PAN, PDA@PAN and Fe^{3+} -PDA@PAN NFAs, and the density and porosity of the samples are summarized in Table 1. All NFAs show ultralight densities below 5 mg cm^{-3} , which translates into high porosities of $> 99\%$. At a small compression stress of 0.1 kPa, the Fe^{3+} -PDA@PAN NFA shows a significantly smaller compression strain than those of PAN and PDA@PAN NFAs, proving that the inter-fiber junctions could indeed lead to more robust 3D NFAs. The difference between the PAN and PDA@PAN NFAs is significant only at relatively high compression strains. Since the mechanical properties of the NFAs are dependent on both the rigidity of each single nanofiber and the presence of inter-fiber junctions, the similar compression mechanical behavior of the PAN and PDA@PAN NFAs at low strains implies that PAN and PDA@PAN nanofibers have similar rigidity. At larger strains, the PDA@PAN NFA shows better compression resistance than the PAN NFA, suggesting that inter-fiber multiple hydrogen bonds may also give inter-fiber junctions in the PDA@PAN aerogels. Thus, the inter-fiber junctions do help to resist deformation under compression stress. This would help to stabilize the highly porous morphology in air filtration. The cyclic compression mechanical behavior of the Fe^{3+} -PDA@PAN cylindrical-shaped NFA was further investigated. In this work, the face velocity of 0.1 m s^{-1} was used in the filtration tests and the NFA exhibits an ultralow density ($< 5 \text{ mg cm}^{-3}$). As a result, the actual compression strain experienced by the filtration material is very small, and hence the strain was set at 5% in the cycling test. As shown in Fig. S3, the compressive stress is only reduced slightly with increasing cycle number, showing the relatively robust structure of Fe^{3+} -PDA@PAN cylindrical-shaped NFA with the ultralow density.

Fig. 7. Typical stress-strain curves of PAN, PDA@PAN, and Fe³⁺-PDA@PAN cylindrical-shaped NFAs. The inset is the digital photograph of 3D PAN, PDA@PAN and Fe³⁺-PDA@PAN cylindrical-shaped NFAs.

Table 1. The density and porosity of the cylindrical-shaped NFAs.

Samples	PAN	PDA@PAN	Fe ³⁺ -PDA@PAN
Density (mg cm ⁻³)	3.32±0.10	3.96±0.39	4.22±0.22
Porosity (%)	99.72	99.67	99.64

To further study the effect of crosslinking on the properties, the samples obtained by the treatment with solutions of much lower (0.025 mg mL⁻¹) and higher (2.5 mg mL⁻¹) Fe³⁺ concentrations, respectively, were also tested, and the results are shown in Table S1 and Fig. S4. Fe³⁺-PDA@PAN-0.025 NFA (Table S1) shows almost the same density and porosity as PDA@PAN NFA (Table 1) owing to very few inter-fiber junctions formed by treating with a solution with very low Fe³⁺ concentration (0.025 mg mL⁻¹). By contrast, Fe³⁺-PDA@PAN-2.5 NFA exhibits a significantly higher density (8 mg cm⁻³) and lower porosity (99.33%) (Table S1) than both PDA@PAN and Fe³⁺-PDA@PAN (Table 1) because of the increased cross-linking degree brought by treating with a solution with a much higher Fe³⁺ concentration (2.5 mg mL⁻¹). The compressive stress of Fe³⁺-PDA@PAN-2.5 is also significantly higher (Fig. S4). It is, however, worth noting that the enhanced compression resistance is accompanied with reduced

porosity, which may cause an increase in pressure drop, which will be discussed in Section 3.4.

3.3. Adsorption behaviors of PAN, PDA@PAN and Fe³⁺-PDA@PAN surface

As we all know, in addition to morphology, surface chemistry is also an important factor affecting the filtration efficiency of an aerogel air filter. To study the effect of surface chemistry on adsorption behaviors of PAN, PDA@PAN and Fe³⁺-PDA@PAN and minimize the influence of morphology, PAN, PDA@PAN and Fe³⁺-PDA@PAN 2D nanofibrous mats, which have similar pore structures, were used for adsorption studies. The morphologies of the PAN, PDA@PAN and Fe³⁺-PDA@PAN 2D mats were examined using SEM after absorption of particles produced by burning incense. In this study, incense smoke was used as model pollutant gas because it contains an amount of substantial ultrafine particles. Liu *et al.* have investigated the composition and surface chemistry of incense PM particles and found that their surface has both polar functional groups (C-O, C=O and C-N) and some non-polar functional groups (C-C, C-H and C=C),³⁴ which well simulate the haze particles generated by biomass burning. In this test, incense was burning continuously in a tube, and the 2D mats were fixed at the bottom of the tube with their upper surface facing the air inlet. A vacuum pump was switched on to force incense smoke flowing down through the mats.

From the SEM images shown in Fig. 8, we could observe that after exposure to incense smoke for 6 min, the surface of the Fe³⁺-PDA@PAN nanofibers on top become much rougher than that of PAN and PDA@PAN nanofibers, indicating that Fe³⁺-PDA@PAN surface adsorbs incense particles more efficiently than PAN and PDA@PAN counterparts. It is worth noting that for PAN and PDA@PAN 2D mats, the adsorption of incense particles occurs much more extensively near the crossing points of the nanofibers. This is because at such locations two fiber surfaces are in close proximity, creating wedge-shaped spaces. Hence, a particle may interact with both surfaces without sacrificing cohesive forces of the particle too much. The adhesion force required for overcoming surface tension is thus smaller. Once some particles are adsorbed at such locations, the fiber surface is modified, facilitating further adsorption.

By contrast, for Fe^{3+} -PDA@PAN, the adsorption occurs intensively throughout each nanofiber, signifying much enhanced interfacial interactions between the fiber surface and particles.

Fig. 8. Typical SEM images of PAN, PDA@PAN and Fe^{3+} -PDA@PAN 2D nanofibrous mats after absorption of PM particles produced by burning incense (absorption time: 6 minutes).

To investigate the reasons for the enhanced adsorption on Fe^{3+} -PDA@PAN surface, Fowke's theory was used to evaluate polarity of PAN, PDA@PAN and Fe^{3+} -PDA@PAN bulk surfaces prepared by spinning coating. According to Fowke's theory, polar and dispersive components of surface energy could be calculated from contact angles. The detailed calculation based on Fowke's theory is explained in the supporting information. Table 2 shows the characterization results for PAN, PDA@PAN, Fe^{3+} -PDA@PAN surfaces with DI water and diiodomethane (CH_2I_2) as the probe liquids. Based on the results given in Table 2, PDA coating could greatly enhance surface polarity, which is due to the functional groups, such as catechol and amine groups, in PDA. For Fe^{3+} -PDA@PAN surface, the polarity is also much higher than that of PAN. The higher polarity benefits PM capture efficiency as the more polar surface will provide stronger dipole-dipole and induced dipole interactions. Moreover, for both PDA@PAN and Fe^{3+} -PDA@PAN, the polar components are much higher than that of PAN while the non-polar components remain almost the same as that of PAN. The

apparent contact angles of PAN, PDA@PAN and Fe³⁺-PDA@PAN NFAs were further measured to support the above analysis. As shown in Fig. S5, PAN NFAs show no significant change in contact angle in 120 s. After PDA coating and Fe³⁺ crosslinking, the apparent contact angles reduce greatly, which are similar to the bulk materials. Moreover, the apparent contact angles of PDA@PAN and Fe³⁺-PDA@PAN NFAs decrease quickly in 30 s. The above analysis could not, however, justify why Fe³⁺-PDA@PAN nanofibers adsorb particles generated by burning incense much more efficiently. Since the analysis did not take electrostatic interaction into consideration, one could deduce that the enhanced adsorption performance of Fe³⁺-PDA@PAN over that PDA@PAN is probably due to the electrostatic interactions brought by ferric ions.

Table 2. Contact angle (CA), overall surface energy (σ_s), polar component (σ_s^P), non-polar component (σ_s^D) and surface polarity of PAN, PDA@PAN, Fe³⁺-PDA@PAN.

Surface	CA (H ₂ O)	CA (CH ₂ I ₂)	σ_s (mN m ⁻¹)	σ_s^P (mN m ⁻¹)	σ_s^D (mN m ⁻¹)	Surface polarity (%)
PAN	49.4	6.8	62.44	12.00	50.44	19.2
PDA@PAN	7.4	11.7	78.08	28.33	49.75	36.3
Fe ³⁺ -PDA@PAN	21.7	7.6	74.92	24.56	50.35	32.8

3.4. Filtration performance

In this study, again the model pollutant particles were generated by burning incense in air. Fig. S6a shows that the incense smoke has a wide mass distribution from 10 nm to around 500 nm, and the particles with sizes between 60 and 400 nm have the highest mass concentration. However, based on the number distribution shown in Fig. S6b, the particles with sizes between 40 nm and 300 nm have the highest number concentration. This difference in size distribution could be attributed to the relatively small mass of the smaller particles, which does not contribute significantly to the total mass aggregate despite there are a large number of such smaller particles.

In air filtration industry, a useful strategy to improve overall filtration performance is to use composite filters.³⁵⁻³⁷ Moreover, for practical applications, a combination of an inexpensive filtration substrate with a thin nanofiber layer may provide superior

filtration performance at a lower cost. In this work, in order to achieve high filtration efficiency and relatively low pressure drop simultaneously, we combined a commercial filtration medium with a very thin layer of 3D NFA. To benchmark the composite filters against commercially available air filters, the filtration efficiencies and pressure drop of a type of commercially HEPA filter (H13) were tested first. H13 filter is composed of polypropylene/glass fibers with diameters ranging from several hundred nanometers to several micrometers, as shown in Fig. S7. The density of H13 is about 275.5 mg cm^{-3} . The filtration efficiencies and pressure drop of a single layer of H13 (H13-1), two layers of H13 (H13-2) and three layers of H13 (H13-3) were tested, respectively. As shown in Table 3, H13-1 exhibits reasonably good efficiencies for PM 0.5, but its efficiency for PM 0.1 is significantly lower. The filtration efficiency here is based on mass percentage, implying that a large number of particles with sizes of tens of nanometers cannot be captured by H13-1. As the number of layers of H13 increases, the filtration efficiencies for PM 0.5 and PM 0.1 all increase, but the pressure drop also increases proportionally with the number of layers. As a result, the QF, which characterizes the overall performance of the filter media by considering both the filtration efficiency and pressure drop, decreases significantly with the number of layers of H13. Thus, ultrafine particles could not be efficiently removed using H13 HEPA filter. Since the highly porous 3D NFAs are specifically designed for capturing ultrafine particles, in this study, a thin layer of 3D NFAs supported by wire mesh is combined with a layer of H13 to improve the filtration efficiency for ultrafine particles (PM 0.1). As shown in Table 3, the addition of a thin layer of PAN, PDA@PAN or Fe^{3+} -PDA@PAN 3D NFAs on H13-1 could improve the efficiency for removing PM 0.5, and in particular PM 0.1. Fe^{3+} -PDA@PAN-H13-1 layer shows the highest efficiencies for PM 0.5 and PM 0.1. More importantly, Fe^{3+} -PDA@PAN-H13-1 exhibits a much lower pressure drop than PAN-H13-1 and PDA@PAN-H13-1, indicating that its multiscale pore structure and enhanced compression resistance indeed help reduce its resistance to airflow significantly. In addition, the filtration efficiency of Fe^{3+} -PDA@PAN-H13-1 for PM 0.1 is higher than those of H13-1 and H13-2, and

comparable to that of H13-3, while its pressure drop is comparable to H13-1, and much lower than H13-2, H13-3. The excellent filtration performance of Fe³⁺-PDA@PAN-H13-1 could be ascribed to its unique surface chemistry and morphological feature, as discussed above.

Table 3. Filtration efficiencies, pressure drop, and QF of the air filters made of different layers of H13 (H13-1, H13-2 and H13-3), as well as a combination of a layer of H13 (H13-1) with PAN, PDA@PAN and Fe³⁺-PDA@PAN NFAs, respectively.

Samples	Filtration efficiency (PM 0.1)	Filtration efficiency (PM 0.5)	Pressure drop (Pa)	QF (PM 0.1)
H13-1	98.28±0.81	99.50±0.01	48.2±4.3	0.084
H13-2	99.67±0.08	99.77±0.00	91.3±7.1	0.063
H13-3	99.86±0.15	99.90±0.02	139.0±6.7	0.047
PAN-H13-1	99.66±0.17	99.71±0.04	82.0±1.4	0.069
PDA@PAN-H13-1	99.64±0.03	99.69±0.01	68.5±7.1	0.082
Fe ³⁺ -PDA@PAN-H13-1	99.72±0.09	99.85±0.02	54.1±3.69	0.110

The filtration performances of Fe³⁺-PDA@PAN-0.025-H13-1 and Fe³⁺-PDA@PAN-2.5-H13-1 were also tested, and the results are shown in Table S1. As expected, Fe³⁺-PDA@PAN-0.025-H13-1 (treated by 0.025 mg mL⁻¹ Fe³⁺ solution), exhibits almost the same filtration performance as PDA@PAN-H13-1 owing to its very low degree of cross-linking. Compared with Fe³⁺-PDA@PAN-H13-1 (treated by 0.25 mg mL⁻¹ Fe³⁺ solution), Fe³⁺-PDA@PAN-2.5-H13-1 (2.5 mg mL⁻¹ Fe³⁺ concentration) shows higher filtration efficiencies for PM 0.1 and PM 0.5 while larger pressure drop. This is due to that Fe³⁺-PDA@PAN-2.5 has more inter-fiber junctions, and hence higher density and lower porosity.

Fig. 9 shows the long-term filtration performance of Fe³⁺-PDA@PAN-H13-1 at the humidity of 60% RH. The pressure drop exhibits almost no change after a

continuous test for 24 h (the fluctuation is within measurement error bar). This reveals the robust structure of Fe^{3+} -PDA@PAN NFA. Moreover, the filtration efficiencies for even ultrathin particles could achieve a high level of >99.5% after testing for 24 h.

Fig. 9. The long-term performance of Fe^{3+} -PDA@PAN-H13-1 at humidity 60% RH.

4. Conclusions

In summary, highly porous yet mechanically robust 3D Fe^{3+} -PDA@PAN NFAs were successfully fabricated via the mussel-inspired approach. The amount of inter-fiber junctions in the Fe^{3+} -PDA@PAN NFAs could be facilely controlled just by adjusting Fe^{3+} concentration. Morphological characterization and compression tests show that both multiple hydrogen bonding provided by PDA coating and Fe^{3+} -PDA coordination bonding could induce the formation inter-fiber junctions, which are suited to construct more robust 3D nanofibrous filters and help stabilize the nanoporous fibrous structure in air filtration processes. Moreover, Fe^{3+} is demonstrated to be both a powerful cross-linking agent and surface chemical modifier for construction of robust 3D NFAs with good adsorption properties towards pollutant particles. The optimized Fe^{3+} -PDA@PAN NFA composited with a layer of commercial HEPA displays higher filtration efficiency for PM 0.1 as well as similar pressure drops in comparison with that of the HEPA filter. Thus, this work opens up the avenue of exploring novel 3D porous aerogels for application in air-cleaning technology.

Notes

The authors declare no competing financial interest.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found online at <https://dx.doi.org/10.1016/j.apsusc.XXXX.XX.XXX>.

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