ZIF-8 Modified Nanofiber Composite Window Screen for Efficient Indoor PM$_{2.5}$ and Formaldehyde Removal

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Abstract: Because people spend a lot of time indoors every day, the presence of particulate matter with a diameter less than 2.5 μm (PM$_{2.5}$) and volatile organic molecular substances in indoor air adversely affect public health. These toxic compounds can be removed from the air using high-efficiency air-filter materials with adsorption capacity. Metal-organic frameworks (MOFs) are among the most suitable materials for air purification as they are synthetic porous materials with excellent adsorption ability. In this study, the zeolitic imidazolate framework-8 (ZIF-8) is uniformly grown on the surface of polyacrylonitrile (PAN) nanofibers using an in situ growth method to prepare ZIF-8@PAN nanofiber composite membranes. The nanofiber composite membrane effectively removes PM$_{2.5}$ and formaldehyde from the air. After loading the optimal amount of ZIF-8, the filtration efficiency of the nanofiber membrane for salt aerosol with a diameter of 0.3 μm increases from 90.3% to 96.9%, and the removal rate of formaldehyde becomes 98% within 20 min in the enclosed space of the laboratory. Moreover, after five repeated tests, the formaldehyde adsorption rate remains above 80%. In addition, ZIF-8@PAN nanofiber membranes are used to fabricate anti-haze window screens, which have great potential to improve indoor air quality and mitigate related health risks.

Keywords: Nanofiber, MOF, Anti-haze, Formaldehyde removal, In situ growth

Introduction

Although the attention of the world and the global health community specifically is deservedly focused on the COVID-19 pandemic, air pollution continues to have large impacts and may also interact with COVID-19 [1]. Among air pollutants, particulate matter with a diameter less than 2.5 μm (PM$_{2.5}$) is the most harmful and can cause various diseases, such as lung cancer, heart failure, and asthma [2], which can result in early death. Even PM$_{2.5}$ may accelerate the propagation speed of COVID-19 [3]. Approximately 1.3 million deaths in China every year are related to long-term exposure to high concentrations of PM$_{2.5}$ [4]. This situation is even more critical in India [5]. In 2020, the annual average concentration of PM$_{2.5}$ in New Delhi reached 84.1 μg m$^{-3}$, which is much higher than the World Health Organization (WHO) recommended limit (10 μg m$^{-3}$). PM$_{2.5}$ in the atmosphere easily penetrates buildings, and as a majority of the population stays indoors most of the time, people often inhale PM$_{2.5}$ indoors [6]. Therefore, controlling the concentration of PM$_{2.5}$ indoors is important for protecting public health. Indoor air contains not only PM$_{2.5}$ but also various volatile organic compounds (VOCs) and other harmful substances. Among the VOCs, formaldehyde is one of the most common pollutants as it is widely found in a variety of furniture, textile, and flooring materials and is recognized as a carcinogen by the World Health Organization [7]. The US National Institute for Occupational Safety and Health (NIOSH) recommended exposure limit (REL) of HCHO is 16 ppb by time-weighted average (TWA), and the permissible exposure limit (PEL) set by the Occupational Safety and Health Act (OSHA) is 0.75 ppm TWA [8].

Currently, two methods are widely used to control indoor PM$_{2.5}$ and formaldehyde levels [9]. The first is to use an air exchange system with a high-efficiency particulate filter [10], which can effectively remove PM$_{2.5}$ from the outdoor air and input the clean air into the room, thereby diluting the indoor formaldehyde concentration. This method effectively purifies the outside air to provide fresh air for the room, but it prohibits the opening of windows for ventilation, which can cause people to feel uncomfortable after a while. The second is an indoor air purification system that uses a composite air filter with an activated carbon layer. This system can quickly remove indoor PM$_{2.5}$ and formaldehyde pollutants [11]. However, this system can only circulate and purify indoor air and cannot supplement fresh air, resulting in insufficient indoor oxygen levels. Moreover, both these methods require the use of fans, which consume a lot of electrical energy during their operation. Additionally, the filters need to be replaced regularly, resulting in high usage costs. Therefore, further studies are required to develop cost-effective methods to reduce indoor PM$_{2.5}$ and formaldehyde levels simultaneously.

Electrospinning technology is widely used in the preparation of nanofiber membranes due to its controllable process, high production efficiency, and low cost. Electrospun nanofiber membranes have the advantages of high porosity, reduced
pressure, large specific surface area, and multiple functions. They are widely used in PM air filtration [12], catalysis [13], water filtration [14], and formaldehyde catalytic oxidation [15]. Air filters with versatility have appeared, such as air filters with photocatalytic activity [16], air filtration nanofiber paper with room temperature catalytic formaldehyde oxidation [17], etc. Due to these advantageous features and the intriguing characteristics of the electrospun nanofibers, electrospinning has attracted much attention to preparing functional air filters. In our previous study, a composite window screen with a sandwich structure was prepared, which consisted of a polyurethane (PU) nanofiber membrane, glass fiber mesh, and polyester fiber mesh as the filter, support, and protective layers. This type of window screen can block PM$_{2.5}$ while maintaining sufficient air permeability and light transmittance [18,19]. In recent years, environmentally friendly materials have attracted more and more attention [20,21]. Such as Jiaxin Cui et al. [22,23] prepared a series of environmentally friendly PVA nanofiber membranes for air filtration by combining electrospinning and hydrogen bond cross-linking technology. The removal efficiency of PM$_{1.0}$ of PVA-tannic acid air filter can reach 99.5% when the pressure drop was only 35 Pa, and the quality factor can reach 0.15 Pa$^{-1}$. Polyacrylonitrile (PAN) electrospun nanofibers are widely used in the field of filtration. The latest research report of Ma et al. shows that the aerogels made of PAN nanofibers not only have the oil/water separation ability but also can be used as pressure sensors [24]. Wenxuan Cao et al. reported that PAN electrospun nanofibers combined with in-situ hydrothermal synthesis method prepared an oil-water separation membrane with photocatalytic activity [25].

In addition, gas separation technology is a good technique for removing formaldehyde from indoors. Metal-organic frameworks (MOFs), a class of hybrid crystalline porous materials, are effective for use in gas separation [26]. MOFs are regular crystal compounds composed of metal particles or clusters as nodes and organic molecules as bridging ligands. Owing to the advantages of large specific surface areas, high porosities, and adjustable pore sizes of MOFs, they are widely used in gas adsorption and separation, catalysis [27], and sensing. Recently, their application in the removal of toxic and harmful substances has become a new focus area of research [28]. However, the fragility of the MOF powders and the difficulty in forming a macroscopic morphology limit their practical applications. Therefore, it is challenging to prepare flexible films from MOF materials. The use of electrospinning technology to fabricate composite nanofibers and MOF materials can overcome these shortcomings and increase the flexibility of MOF materials.

In this study, composite membranes comprising PAN nanofibers loaded with zeolitic imidazolate framework-8 (ZIF-8) (one of the most stable MOFs) were prepared by a two-step method of fiber doping and in situ growth. This composite material exhibits excellent filtration (with high efficiency and low resistance) and gas-adsorption performances. To demonstrate the practical application of this material, the as-prepared nanofiber composite membrane was used to fabricate a window screen, which provides indoor ventilation while simultaneously removing PM$_{2.5}$ and absorbing formaldehyde from indoors. As a new type of composite filter material, it has immense potential for applications in the field of air purification.

**Experimental**

**Experimental Materials**

PAN (Mw=150000, Shaoxing Gimel Composite Material Co., Ltd.); N,N-dimethylformamide (DMF; analytical grade, China National Pharmaceutical Group Co., Ltd.); Zn(CH$_3$COO)$_2$·2H$_2$O (analytical grade, Tianjin Kemiu Chemical Reagent Co., Ltd.), 2-Methylimidazole (2-MI, analytical grade, Tianjin Kemiu Chemical Reagent Co., Ltd.); ethanol (analytical grade, Tianjin Fuyu Chemical Company); formaldehyde (Xilong Science); nonwoven PET (25 g m$^{-2}$, Zhenguou Yuli New Material Technology Co., Ltd.) were used as the base materials in this study.

**Preparation of Spinning Solutions**

The PAN raw material was placed in an oven (PH-010A, Zhejiang Hengyue Instrument Co., Ltd.) and dried at 60 °C for 6 h. First, the electronic balance weighs PAN powder (FA1004B, Shanghai Youyi Instrument Co., Ltd.). PAN powder was dissolved in DMF and stirred with a magnetic stirrer (MYP12-2-100W, Shanghai meiyingpu Instrument Co., Ltd.) and dried at 60 °C (Beijing Yong Lang Le Ye Co., Ltd.). The spinning distance fraction of zinc acetate (6, 8, or 10 wt.%) were added to the as-prepared PAN spinning solutions (25 g m$^{-2}$, Zhenguou Yuli New Material Technology Co., Ltd.) at 60 °C for 8 h to prepare a PAN spinning solution with a mass fraction of 8, 10, 12, 14, or 16 wt.%. To prepare the Zn(CH$_3$COO)$_2$/PAN spinning solutions, the same steps were followed, but different mass fractions of zinc acetate (6, 8, or 10 wt.%) were added to the 12 wt.% PAN solution.

**Preparation of Nanofiber Membranes**

The Zn(CH$_3$COO)$_2$/PAN nanofiber membrane was prepared using customized electrospinning equipment (Beijing Yong Lang Le Ye Co., Ltd.). The spinning distance and spinning voltages were 18 cm and 30 kV, respectively. The Zn(CH$_3$COO)$_2$/PAN nanofiber membrane was immersed in an absolute ethanol solution of 2-MI (2 g of 2-MI was dissolved in 100 ml ethanol solution) for 24 h. The Zn(CH$_3$COO)$_2$/PAN nanofiber membrane was then cleaned with ethanol and water and placed in an oven at 60 °C to dry completely.

**Spinning Solution Viscosity Measurement**

The viscosity of the Zn(CH$_3$COO)$_2$/PAN spinning solutions was measured using a digital viscometer (RVDV-I, Shanghai Yueping Scientific Instrument Co., Ltd.) at a
temperature of 25 °C and 30 % relative humidity. For each test, 25 mL of the homogeneous solution was used.

Characterization of the Nanofibers

The morphology of the nanofibers was characterized using a desktop scanning electron microscope (Phenom Pure desktop scanning electron microscope, Phenom-Scientific instruments Co., Ltd., SEM) and a field emission scanning electron microscope (Zeiss SIGMA-500, Shanghai Baimao Instrument Technology Co., Ltd., FE-SEM) at a voltage of 5 kV after the sample was coated with gold. The growth of ZIF-8 crystals on the nanofibers was observed using Transmission Electron Microscopy (TEM). An FE-SEM equipped with an Energy-dispersive X-ray spectrometry (EDS) system was used to analyze the elemental composition of the samples. The crystalline structure of ZIF-8 was detected using X-ray diffraction (XRD, Bruker D8, Bruker (Beijing) Technology Co., Ltd.) with a Cu Kα radiation source at 40 kV and 30 mA over a 2θ range of 5 °-50 °. The compositions of the prepared samples were examined using X-ray Photoelectron Spectroscopy (XPS). Atomic Force Microscopy (AFM, MFP-3D Infinity) was used to characterize the morphology and \( R_a \) of the sample in tapping mode with a scan range of 0-5 \( \mu m \). The functional group information and material structure of the composite nanofiber membrane materials were analyzed using Fourier transform infrared spectrometry (FT-IR, Nicolet Nexus 670) over a scanning range of 400-4000 cm\(^{-1}\). The specific surface area and pore diameter distribution were conducted using Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) based on \( N_2 \) adsorption-desorption examination method (AUTOSORB-IQ, China).

Particulate Matter Filtration Tests

An automatic filter tester (TSI 8130A, Suzhou Huayu Purification Equipment Co., Ltd.) was conducted to study the filtration efficiency and pressure drop of the samples. Monodisperse charge-neutralized NaCl aerosol particles with a mass median diameter of 0.3 \( \mu m \) and a geometric standard deviation of < 1.86 were generated from a 2 wt.% NaCl aqueous solution and then fed into the filter holder. The airflow with particles passed through the sample with an effective testing area of 100 cm\(^2\) at a velocity of 5.3 cm\(^{-1}\) (volumetric flow rate: 32 L/min). The quality factor (QF) is a comprehensive index of material filtration performance and is defined as equation (1) [29,30]:

\[
QF = \frac{-\ln(1-\eta)}{\Delta p}
\]

In equation (1), \( \eta \) and \( \Delta p \) are the filtration efficiency (%) and filtration resistance (Pa).

Formaldehyde Adsorption Performance Tests

A custom confined jar was prepared for the formaldehyde adsorption performance measurements. Formaldehyde solution was diluted with deionized water at a ratio of 1:50, and the mixture was sprayed in the jar during each test. A formaldehyde tester (VXV100-CH2O-G, Shenzhen ruikailei Technology Co., Ltd.) was used to observe the changes in the formaldehyde content in the jar in real-time, as shown in Figure 1. When the detection data of the formaldehyde tester stabilized, a membrane sample with an area of 25×25 cm\(^2\) was placed in the jar, and then the formaldehyde adsorption performance test of the material was started. The formula for calculating the formaldehyde removal rate (Q, %) was as equation (2) [31]:

\[
Q = \frac{C_0 - C_1}{C_0} \times 100\%
\]

In equation (2), \( C_0 \) is the initial concentration of formaldehyde (mg m\(^{-3}\)). \( C_1 \) is the final concentration of formaldehyde (mg m\(^{-3}\)).

Results and Discussion

Morphology of PAN Nanofibers

The viscosity of the spinning solution used to prepare the PAN fibers was analyzed. Table 1 shows the viscosity of spinning solutions with different PAN concentrations; as the concentration of PAN in the solution increased, the viscosity of the solution also increased.

The concentration of the spinning solution affects the morphology of the electrospun nanofibers. In the case of the

| PAN concentration (wt.%) | Average viscosity (mPa s) |
|-------------------------|--------------------------|
| 8                       | 246                      |
| 10                      | 337                      |
| 12                      | 486                      |
| 14                      | 531                      |
| 16                      | 559                      |

![Figure 1. Self-built formaldehyde detection device.](image-url)
solution with a low concentration (8 wt.%). This is because the molecular chain is not sufficiently strong to effectively resist the action of the electric field applied during spinning, causing it to break. In addition, because of the viscoelastic effects of polymer molecular chains, the polymer solutions tend to shrink, which leads to the agglomeration of molecular chains and the formation of beads. During the electrospinning process, beads may also be produced owing to the inhomogeneous forces. When the solution concentration was increased to 10 wt.%, the number of beads decreased, and the bead shape changed from round to oval (Figure 2(b)). With a further increase in the solution concentration to 10, 12, 14, and 16 wt.%, the viscosity of the solution increased, resulting in the solution being fully stretched in the applied electric field, and continuous nanofibers were formed without beads (Figures 2(b-e)). The average fiber diameter increased with the solution concentration (Figure 2(f)). The orientation of the molecular chains in a more viscous solution requires a greater electric field force to form a larger fiber diameter. The average diameters of the nanofibers were 127 nm, 130 nm, 188 nm, 223 nm, and 305 nm for 8 wt.% solutions, 10 wt.% solutions, 12 wt.% solutions, 14 wt.% solutions, and 16 wt.% solutions, respectively. Because the morphology and diameter of the PAN nanofibers affect the subsequent growth of the ZIF-8, nanofibers with 12 wt.% PAN were selected for further experiments.

Morphology of Zinc Acetate/PAN Nanofibers
ZIF-8 crystals were formed by the coordinated combination of Zn$^{2+}$ and the organic ligand 2-MI. Zinc acetate (Zn(CH$_3$COO)$_2$) particles were added to the PAN solution, and Zn(CH$_3$COO)$_2$/PAN nanofibers were then prepared via electrospinning to obtain fibers with Zn$^{2+}$ as a precursor for forming ZIF-8. As shown in Figure 3, After adding Zn(CH$_3$COO)$_2$ at a concentration of 6 wt.%, 8 wt.%, or 10 wt.%, the average diameter of the prepared nanofibers increased to 473, 487, or 497 nm, respectively. This may be because Zn(CH$_3$COO)$_2$ affects the solubility of PAN, which increases the degree of molecular chain entanglement, increasing the solution viscosity and corresponding increase in the fiber diameter. The addition of Zn(CH$_3$COO)$_2$ did not destroy the structure of the PAN nanofibers, and the surface of the fibers was smooth without beads.

Morphology of ZIF-8@PAN Nanofiber Membranes
Soak Zn(CH$_3$COO)$_2$/PAN nanofiber membrane in 2-MI ethanol solution to prepare ZIF-8@PAN nanofiber membrane. As shown in Figure 4, Zn(CH$_3$COO)$_2$/PAN nanofiber membranes were soaked in 2-MI, during which Zn$^{2+}$ on the PAN nanofibers undergoes a coordination reaction with the 2-MI ligand. Subsequently, ZIF-8 crystals were grown in situ on the surface of the PAN nanofibers. The prepared ZIF-8@PAN nanofiber membrane had good flexibility and could be folded and bent, indicating that this material has good development potential for various applications. The materials obtained by immersing the 6 wt.% Zn(CH$_3$COO)$_2$/12 wt.%
PAN, 8 wt.% Zn(CH$_3$COO)$_2$/12 wt.% PAN, and 10 wt.% Zn(CH$_3$COO)$_2$/12 wt.% PAN nanofiber membranes in the 2-MI soaking solution were named ZIF-8@PAN-6, ZIF-8@PAN-8, and ZIF-8@PAN-10 respectively. The morphology of the ZIF-8@PAN nanofibers was characterized using SEM (Figure 5). The nanofiber structure was not destroyed after growing ZIF-8. After soaking, the diameter of the fibers increased, and the average diameters were 594 nm, 605 nm, and 645 nm for ZIF-8@PAN-6, ZIF-8@PAN-8, and ZIF-8@PAN-10, respectively. This increase in diameters was a result of the growth of a dense layer of ZIF-8 crystals on the surface of the PAN nanofibers, and the surface of the fibers changed from smooth to rough. The surfaces of some ZIF-8@PAN-6 nanofibers were slightly convex (Figure 5(a)). With the increasing concentration of Zn(CH$_3$COO)$_2$ on the PAN nanofiber, dense crystals were observed on the surface of the ZIF-8@PAN-8 nanofibers (Figure 5(b)). When the concentration of Zn(CH$_3$COO)$_2$ increased to 10 wt.%, the
Figure 5. SEM images and fiber diameter distributions of (a) ZIF-8@PAN-6, (b) ZIF-8@PAN-8, and (c) ZIF-8@PAN-10 nanofiber membranes.

Figure 6. (a-c) SEM images of a ZIF-8@PAN-8 nanofiber membrane at different magnifications, (d-g) EDS Elemental maps of a ZIF-8@PAN-8 nanofiber membrane, (h-j) TEM images of a ZIF-8@PAN-8 nanofiber at different magnifications, (k) AFM image, and (l) extracted three-dimensional (3D) image of a ZIF-8@PAN-8 nanofiber membrane.
crystals on the surface of ZIF-8@PAN-10 nanofibers agglomerated, and about 2 μm crystals were observed at the intersections and gaps between the fibers. This may be due to the high content of Zn(CH₃COO)₂ in the fiber.

The morphology of the ZIF-8@PAN-8 nanofiber membrane was characterized using field emission SEM (FE-SEM). ZIF-8 crystals were observed on the PAN nanofiber surface as a dense crystal layer that coated the PAN nanofibers (Figures 6(a-c)). EDS maps (Figures 6(d-g)) showed that C, N, O, and Zn were distributed in the PAN nanofibers. The uniform distribution of Zn confirmed the successful growth of ZIF-8 crystals on the PAN nanofibers. The TEM analysis of the ZIF-8@PAN-8 nanofibers showed triangular crystals emerging from the surface of PAN fibers, which further confirmed the growth of ZIF-8 crystals on the PAN nanofibers (Figures 6(h-j)). To investigate the roughness of the ZIF-8@PAN-8 nanofiber membrane, AFM in the tapping mode was used to characterize the surface of the nanofiber membrane (Figures 6(k,l)). The AFM images also showed the closely arranged crystals on the fiber surface, which was consistent with the FE-SEM, EDS, and TEM results. The valleys and peaks in the thickness direction of the nanofiber membrane material were represented by the depth of the color change in the AFM and corresponding extracted 3D images. The ZIF-8@PAN-8 nanofiber membrane had a high surface roughness \((R_a)\) of 307 nm. This is because the surface of the ZIF-8@PAN-8 nanofiber membrane was composed of a one-dimensional nanomaterial (PAN nanofibers) with staggered random stacking as the skeleton structure and a secondary nanostructure (ZIF-8 crystals) on the fiber surface. The loading of the ZIF-8 crystals increased the \(R_a\) of the PAN nanofiber membrane, which may increase the effective surface area and is beneficial for filtration applications using the nanofiber membrane and enhance its microparticle capture performance.

**Structure of ZIF-8@PAN-8 Nanofibers**

The crystal structure and crystallinity of the ZIF-8@PAN-8 nanofibers were determined using XRD. Figure 7(a) shows the XRD patterns of ZIF-8, PAN, and ZIF-8@PAN-8. The XRD pattern of the synthesized ZIF-8 crystals matched well with the simulated pattern with peaks at 7.25 ° (011), 10.30 ° (002), 12.65 ° (112), 14.60 ° (022), 16.40 ° (013), 17.95 ° (222), 22.05 ° (114), 24.32 ° (233), 25.42 ° (224), 26.50 ° (134), 29.48 ° (044), 30.42 ° (334), 31.33 ° (244), and 32.27 ° (235) [32]. The XRD pattern of the ZIF-8@PAN-8 nanofiber membrane before and after immersion in 2-MI.

![Figure 7](image-url)
PAN-8 nanofibers was similar to that of ZIF-8, indicating that ZIF-8 grew abundantly on the PAN nanofibers. The diffraction peaks of the ZIF-8@PAN-8 nanofibers also indicate that the ZIF-8 crystal grown on the PAN nanofibers formed a continuous and dense crystal layer. The surface chemical elements of the prepared ZIF-8@PAN-8 nanofibers were analyzed by XPS. The XPS full spectrum of ZIF-8@PAN-8 (Figure 7(b)) exhibits peaks at 532.03 eV, 399.68 eV, and 286.33 eV corresponding to O 1s, N 1s, and C 1s, respectively, and peaks at 1022.08 eV and 1045.08 eV corresponding to Zn 2p$_{3/2}$ and Zn 2p$_{1/2}$, respectively [33,34]; thus indicating that ZIF-8 was well-formed on the PAN nanofibers, which is consistent with the EDS and XRD results. To further prove the existence of each component in the ZIF-8@PAN-8 membrane, FT-IR spectra of PAN, ZIF-8, and ZIF-8@PAN-8 were recorded (Figure 7(c)). In the FT-IR spectrum of PAN, the stretching vibration peak of -C≡N at 2240 cm$^{-1}$ represented the characteristic peak of the cyano group in PAN. The absorption peak at 1453 cm$^{-1}$ was due to the stretching vibration of -C=C-, and the peak at 2946 cm$^{-1}$ was ascribed to the stretching vibration of -C-H in -CH and -CH$_2$ [35]. The FT-IR spectra of ZIF-8@PAN-8 had characteristic peaks of ZIF-8, in addition to those of PAN. The absorption peaks at 1314 and 1143 cm$^{-1}$ were due to the stretching vibration of the C-H bond of 2-MI [36]. The peak at 1380 cm$^{-1}$ was due to the stretching vibration of the C-C bond and those at 1681 and 1573 cm$^{-1}$ were due to the stretching vibration of the C=N bond. The peaks at 1426, 1143, and 994 cm$^{-1}$ were due to the stretching vibration of the C=N bond; the peak at 3140 cm$^{-1}$ was due to the stretching vibration of the N-H bond, and the peaks at 756 cm$^{-1}$ and 689 cm$^{-1}$ were due to the out-of-plane vibration of the imidazole ring [37]. The FT-IR spectrum further showed that the coordination reaction between 2-MI and Zn$^{2+}$ generated the ZIF-8 crystals on the fiber. Furthermore, the Zn(CH$_2$COO)$_2$/PAN, ZIF-8@PAN-6, ZIF-8@PAN-8, and ZIF-8@PAN-10 nanofiber membranes were weighed using an electronic balance (Figure 7(d)). The weight change of the nanofiber membrane after immersion corresponds to the number of ZIF-8 crystals grown on the PAN nanofibers.

**Filtration Performance of ZIF-8@PAN Membranes**

The filtration performances of pure PAN, Zn(CH$_2$COO)$_2$/PAN, ZIF-8@PAN-6, ZIF-8@PAN-8, and ZIF-8@PAN-10 nanofiber membranes were tested using a TSI8130-A automatic filter material detector. Figure 8(a) shows that the pure PAN nanofiber membrane had a filtration efficiency of 90.3 %, filtration resistance of 53.5 Pa, and QF of 0.0436 Pa$^{-1}$. The Zn(CH$_2$COO)$_2$/PAN nanofiber membrane had a filtration efficiency of 93.5 %, filtration resistance of 60.7 Pa, and QF of 0.0450 Pa$^{-1}$. The decrease in filtration efficiency was due to the addition of Zn(CH$_2$COO)$_2$, which resulted in an increase in the nanofiber diameter and a decrease in the pore size. The ZIF-8 crystals increase the active surface area between the PAN nanofiber membrane and microparticles, and subsequently the effective filtration area of the fiber membrane surface increases (consistent with the AFM analysis). This increases the capture performance of the microparticles and a corresponding increase in the filtration efficiency. The enhanced filtration performance of the ZIF-8@PAN nanofiber membrane was also attributed to its stronger electrostatic force. Since the outer surface of PM$_{2.5}$ pollutant particles contains polar functional groups, such as C-O, C=O, C-N, the metal ions and defects in ZIF-8 generate unbalanced potential, which makes the polar PM$_{2.5}$ surface polarized and enhances the electrostatic effect [38]. When the concentration of Zn(CH$_2$COO)$_2$ was 6 wt.%, the filtration efficiency of the ZIF-8@PAN-6 nanofiber membrane was 93.5 %, the filtration resistance was 60.7 Pa, and the QF was 0.0450 Pa$^{-1}$. When the Zn(CH$_2$COO)$_2$ concentration was increased to 8 wt.%, the filtration efficiency of the ZIF-8@PAN-8 nanofiber

![Figure 8.](image-url)
membrane reached 96.9 %, with a filtration resistance of 65.8 Pa and the QF of 0.0528 Pa\(^{-1}\). With increasing ZIF-8 loading, the crystals grew on the surface of the PAN nanofibers aggregated. Large crystals were observed at the intersections and gaps between the fibers, which reduced the pore size of the fiber membrane and increased the filtration resistance. The filtration efficiency of the ZIF-8@PAN-10 nanofiber membrane was 97.1 %, with a filtration resistance of 76.2 Pa and a QF of 0.0465 Pa\(^{-1}\).

**Formaldehyde Adsorption Performance of ZIF-8@PAN Membranes**

The formaldehyde adsorption properties of the PAN and ZIF-8@PAN nanofiber membranes were analyzed. The initial concentration of formaldehyde in the device was approximately 2 mg m\(^{-3}\). As evident from the decrease in formaldehyde concentration over time (Figure 9(a)), compared with the pure PAN nanofiber membrane, the ZIF-8@PAN nanofiber membrane had a larger formaldehyde adsorption capacity. The pure PAN nanofiber membrane decreased the formaldehyde concentration from 1.95 mg m\(^{-3}\) to 1.18 mg m\(^{-3}\) over 2 h (removal rate of 41.3 %) while the ZIF-8@PAN-8 nanofiber membrane reduced the formaldehyde concentration to 0.04 mg m\(^{-3}\), showing an excellent formaldehyde adsorption performance. Compared with pure PAN, ZIF-8@PAN nanofibers have better formaldehyde adsorption performance. The possible mechanism is: on the one hand, the loading of ZIF-8 increases the specific surface area of PAN [39]. On the other hand, the electrostatic adsorption of ZIF-8 with formaldehyde also leads to the improvement of formaldehyde adsorption performance [40].

The formaldehyde adsorption rates of the ZIF-8@PAN-6, ZIF-8@PAN-8, and ZIF-8@PAN-10 nanofiber membranes were 92.9 %, 98.0 %, and 95.0 %, respectively (Figure 9(b)). With increasing Zn(CH\(_3\)COO)\(_2\) content in the PAN nanofibers, the loading content of ZIF-8 increased after soaking, and the formaldehyde adsorption performance was enhanced. However, there was an optimal Zn(CH\(_3\)COO)\(_2\) content. When the content of Zn(CH\(_3\)COO)\(_2\) was 10 wt.%, the ZIF-8 crystals on the PAN nanofibers showed partial aggregation, which reduced the adsorption of formaldehyde. This is because the agglomeration of ZIF-8 particles leads to the decrease of the specific surface area of the fiber, which further leads to the decrease of the formaldehyde adsorption rate. For formaldehyde adsorption materials, reusability is important for practical applications. Based on the experiments performed here, the ZIF-8@PAN-8 nanofiber membrane showed an excellent comprehensive performance. Therefore, the reusability of the ZIF-8@PAN-8 nanofiber membrane was analyzed by cyclic formaldehyde adsorption tests. Like

![Figure 9](image-url)
most adsorption materials, the adsorption performance of the ZIF-8@PAN-8 nanofiber membrane decreased gradually after the cyclic adsorption test. From the adsorption curve of the ZIF-8@PAN-8 nanofiber membrane, the time to reach the inflection point is gradually prolonged (Figure 9(c)). This indicates that during the cyclic adsorption test, the first residual formaldehyde in the pore will form competitive adsorption with the second formaldehyde. The formaldehyde removal rate decreased with increasing cycle number (98.0 %, 94.9 %, 91.0 %, 86.2 %, and 81.5 % for five sequential formaldehyde adsorption cycles; Figure 9(d)). However, the membrane maintained a sufficiently high formaldehyde adsorption capacity.

**Figure 10.** Pore size distribution and surface areas of ZIF-8, PAN membranes, and ZIF-8@PAN-8 nanofiber membranes.

**Figure 11.** (a) Composite nanofiber window screen, (b) drawing of window screen structure, (c) SEM image and diameter distribution of nanofiber layer, (d) PM$_{2.5}$ test purifying device, and (e) PM$_{2.5}$ value change of filter material in filtering air at different times.
Specific Surface Area and Pore Size Distribution of Nanofibrous Membranes

The specific surface area of the prepared materials was determined by nitrogen adsorption and desorption. According to the pore size distribution image, the pore size of ZIF-8 is at the micropore level, and PAN membranes contain almost no micropores. However, the micropore size distribution of ZIF-8@PAN-8 membranes is more than that of PAN membranes. This is due to the loading of ZIF-8 on PAN nanofibers, implying the more gas transmission channels of ZIF-8@PAN-8 membranes for gas adsorption. In addition, the Brunauer-Emmett-Teller (BET) surface area of ZIF-8@PAN-8 membranes was calculated to be 211 m² g⁻¹, much higher than that of the PAN membranes, mainly due to the large increase in the number of micro/mesopores provided by the loading of ZIF-8 on the surface of PAN nanofibers (Figure 10). The higher surface area of ZIF-8@PAN-8 membranes facilitates gas adsorption.

Application of Membranes as Multifunctional Window Screens

The structure of the window screen made from nanofiber membranes is shown schematically in Figures 11(a-c). Considering that the airflow occurs from outdoors to indoors, the first layer is a glass-fiber screen; the middle layer is the ZIF-8@PAN nanofiber membrane, and the final layer is a nonwoven polyester (PET) layer. To compare the layer is the ZIF-8@PAN nanofiber membrane, and the final layer is a glass-fiber screen; the middle layer is a nonwoven polyester (PET) layer. The higher surface area of ZIF-8@PAN-8 membranes facilitates gas adsorption.

Conclusion

In this study, Zn(CH₃COO)₂ was doped into a PAN spinning solution to prepare Zn(CH₃COO)₂/PAN nanofibers. After soaking, the ZIF-8 crystal layer was grown on PAN nanofibers by in-situ polymerization with 2-methylimidazole. The uniformity of ZIF-8 can be controlled by controlling the doping amount of Zn(CH₃COO)₂. Due to the existence of ZIF-8, ZIF-8@PAN nanofiber membrane has better filtration performance than pure PAN nanofiber membrane (quality factor increased from 0.0436 Pa⁻¹ to 0.0528 Pa⁻¹) and also has good formaldehyde adsorption performance (2 mg m⁻³ formaldehyde concentration can be reduced by 98 % within 2 hours, after 5 cycles of testing, it can still maintain more than 80 % filtration performance). The in-situ immersion growth method is simple and quick, and it can be predicted that this method will be widely used in multifunctional air filter materials. And ZIF-8@PAN nanofiber membrane has good filtration performance and can absorb formaldehyde. It can be predicted that this kind of nanofiber material will be widely used in the field of indoor air purification, such as window screens.

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