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Bumpy structured nanofibrous membrane as a highly efficient air filter with antibacterial and antiviral property

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HIGHLIGHTS
• Higher filter efficiency and lower pressure drop due to bumpy nanorough structure.
• Excellent antibacterial property against Escherichia coli and Staphylococcus aureus. Antiviral property against Porcine Deltacoronavirus.
• Antiviral property against Porcine Deltacoronavirus.
• Simultaneously capturing multiple air pollutants: NO₂, SO₂, and some VOCs.

GRAPHICAL ABSTRACT

ABSTRACT
Recently, the pandemic infectious diseases caused by coronavirus have prompted the development of air filter membranes to against infectious agents and protect human health. This research focuses on air filter membrane with antibacterial and antiviral property for high-efficiency particulate matter (PM) removal. Herein, polyamide-6 electrospun nanofibers were anchored with silver nanoparticles through hydrogen-bond. Bumpy nanorough surface and multilevel structure contribute to improve capture capacity, and silver nanoparticles provide a strong ability to inactivate bacteria and virus. In conclusion, this membrane exhibits high PM2.5 filtration efficiency of 99.99% and low pressure drop of 31 Pa; simultaneous removal of multiple aerosol pollutants, e.g., SO₂, NO₂, methylbenzene, L-Nicotine; superior antibacterial performance against Escherichia coli (Gram negative bacteria) and Staphylococcus aureus (Gram positive bacteria), antiviral property against Porcine Deltacoronavirus and not significant cytotoxicity. Research of air filtration material is important to remove air pollutants and to prevent infection and spread of respiratory infectious diseases.

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1. Introduction
Recent years, the pandemic infectious diseases have become urgent issues, caused by various coronavirus, including severe acute respiratory syndrome coronavirus-2 (SARS-CoV-2), SARS-CoV and Middle East respiratory syndrome coronavirus (MERS-CoV) (Walls et al., 2020; Guan et al., 2003; Zumla et al., 2015). According to the latest research, SARS-CoV-2 may have the potential via aerosols to be transmit in addition to via droplets spread in air. And aerosols mainly exist in two size ranges: submicron region (0.25 to 1.0 μm) and supermicron region (>2.5 μm) (Liu et al., 2020). It was also reported that PM2.5 could be carriers of bacteria, viruses and organic pollutants (Yang et al., 2020a). More seriously, PM2.5 can be suspended in the atmosphere for a long time and steadily penetrate into human organs through respiratory system, causing hazardous effects on respiratory and cardiovascular system (Anderson et al., 2012; Pope III et al., 2011). This issue prompts the discovery and development of filter membranes with good...
antimicrobial and antiviral property, applied to masks, personal protection gear, or medical breathing filters.

Nanofibrous membrane prepared by electrospinning technique has been under vast research for air filter membrane (Li et al., 2019; Barhoum et al., 2019; Zhu et al., 2017). The electrospun nanofibrous membranes (ENMs) with fine diameter, high porosity and high surface-to-volume ratio can significantly intercept the fine particulate, which contribute to high filtration efficiency and low pressure drop (Han et al., 2019; Yang et al., 2020b). Y Cui’s group found out that polar polymer nanofiber, such as polyacrylonitrile (PAN), polyamide (PA), displayed better affinity to PM$_{2.5}$ pollutants than nonpolar polymer nanofiber, for instance, polystyrene (PS), polypropylene (PP), etc. (Liu et al., 2015; Xu et al., 2016). PA6, a typical polar polymer, is a promising suitable candidate as air filter material. Polar polymer ENMs have higher filtration efficiency and lower pressure drop for PM$_{2.5}$. However, it still need more effort to effectively filter submicron ultrafine particles, owing to the limited short-range intermolecular force of polar polymer (Zhang et al., 2020). In related applications, ventilator breathing systems and medical masks also need to be well filtered to remove ultrafine submicron particles or nano-aerosols (Akhtar et al., 2020; Leung and Sun, 2020). Therefore, it is necessary to develop the filter membranes for submicron ultrafine particles that should achieve simultaneously high filtration efficiency and low pressure drop.

Constructing bumpy rough structure is an effective strategy to achieve high efficiency and low pressure drop for submicron ultrafine particles due to the effective surface area and the surface roughness. Rough surfaces formed by convex, creased or wrinkled region create the non-slip and stagnation of aerosol particles on the surface of fibers leading to excellent filter performance (Wang et al., 2014; Al-Attabi et al., 2019; Li et al., 2018). Further, surface modification of electrospun nanofibers with nanoparticles was found to be an easy and effective way to construct structures on surface (Zhu et al., 2018; Su et al., 2017). But the stability of nanoparticles on fibers is still worth considering, because circulation of released nanoparticles in air is harmful. As reported, metal nanoparticle is easy to control and modify stably the nanofiber surface by hydrogen-bonding interactions (Dong et al., 2008). Nanoparticles not only contribute to enhance the filter performance, but also provide other functions, such as antibacterial property (Vanangamudi et al., 2015; Bortolassi et al., 2019), magnetic property (Kim et al., 2017), photocatalytic activity etc. (Su et al., 2017). Silver nanoparticle (Ag NP) is a typical inhibitory and bactericidal, disinfectant (Deshmukh et al., 2019), which has been applied on electrospun nanofibers. However, Ag NPs aggregation is still worth considering, because it may decrease in antimicrobial efficiency (Bortolassi et al., 2019). Hwang’s group has used spark discharge generation system to synthesize Ag NPs, that were applied to the commercial air filter for antiviral ability to MS2 and H1N1 virus (Joe et al., 2016; Park et al., 2020). Their research suggests the feasibility of using Ag NPs on air filtration against viruses. However, now it still need more researches on nanofibrous membrane simultaneously with high filtration efficiency and low pressure drop, antibacterial and antiviral property.

Herein, we found a suited strategy to meets the requirements of high efficiency filtration, antibacterial and antiviral property at the same time (Scheme 1). Through electrospinning technique, PA6 nanofibrous membrane was prepared on the PP nonwoven substrate then assembled Ag NPs via impregnation method. The impact of the membrane structure was investigated and correlated to the air filtration performance. Escherichia coli (E. coli), as a typical Gram negative bacteria, and Staphylococcus aureus (S. aureus), as a Gram positive typical bacteria, were utilized to assess the antibacterial activity of air filter membranes. Porcine Deltacoronavirus (PDCoV) is an enveloped, single-stranded, positive-sense RNA virus, belonging to Coronaviruses (Zhang, 2016; He et al., 2020), which was used to evaluate antiviral property of the membranes. We believe that air filter material with high efficiency filtration, antiviral and antibacterial property is important to capture air pollutants and to prevent infection and spread of respiratory infectious diseases.

2. Materials and methods

2.1. Materials

PA6 ($M_\text{w} = 15,000–20,000$, CAS No. 24993-04-2) was purchased from Toray industries (Japan). PP (CAS No. 9003-07-0) nonwoven substrate was brought from Shandong Taipeng group Co., Ltd. (China). Formic acid (HCOOH, CAS No. 64-18-6), hydrochloric acid (HCl, CAS No. 7647-01-0), sodium citrate (Na$_3$C$_6$H$_5$O$_7$·2H$_2$O, CAS No. 68-04-2) and agar powder (CAS No. 9002-18-0) were available from Sinopharm Chemical Reagent Co., Ltd. (China). Silver nitrate (AgNO$_3$, CAS No. 7761-88-8) was purchased from Shanghai Qiangshun Chemical Reagent Co., Ltd. (China). Nutrient Broth (NB) and Tryptic Soy Broth (TSB) was gotten from Beijing Land Bridge Technology Co., Ltd. (China). MTTS (CAS No. 2348-71-2), Glutaric dialdehyde (CAS No. 111-30-8) and Dimethyl sulfoxide (DMSO, C$_3$H$_7$OS, CAS No. 67-68-5) all supplied by Biosharp (China). All chemicals were used without further purification.

![Scheme 1. Schematics showing PA6@Ag ENM as an air filter membrane with antibacterial and antiviral property.](image-url)
2.2. Electrospinning

PA6 solution was prepared by dissolving 1.3 g nylon 6 in 8.7 g formic acid with continuous magnetic stirring for 2 h at room temperature. The distance between needle and sample collector, voltage, processing temperature, and average flow rate were 18 cm, 18 kV, 40 °C, 0.5 mL/h, respectively. In evaluation of filtration performance, to determine optimum basis weight of membranes, the electrospinning time was controlled at 5 min, 10 min, 15 min, 30 min, 45 min, 60 min, respectively. The electrospun nanofibers were deposited on PP substrate, then peeled off from the roller collector.

2.3. Assembly of Ag NPs on PA6 nanofiber

Ag NPs were synthesized by sodium borohydride reduction of silver nitrate in the presence of sodium citrate as a stabilizing reagent. 18 mg silver nitrate, 20 mg sodium citrate and 45 mL distilled water were added into flask, with 5 mL 4 mg/mL sodium borohydride aqueous solution added dropwise under strong magnetic stirring for 1 h. In this way, Ag NPs were obtained, then the pH value of Ag colloidal solution was adjusted from 9 to 7, 5, 3 by HCl. PA6/PP membrane was immersed in the Ag solution for another 3 h. After the impregnation, the Ag-loaded membrane was taken out, rinsed in deionized water for three times and dried at room temperature.

2.4. Evaluation of PM filtration performance

A TSI Model 8130 Automated Filter Tester was bought from Huada Filter Technology Co., Ltd. China. It was used to measure the air filtration performance: filter efficiency and pressure drop. The device is attached to a particle generator which generates charge neutralized micron monodisperse solid Sodium chloride (NaCl) particles of 0.3–10.0 μm in diameter. The aerosol concentration and size distribution at the upstream and downstream of the filters were measured by two solid-state laser photometers. The pressure transmitter was utilized to measure the pressure drop of the filters. All NaCl aerosol tests were conducted at room temperature with a continuous air flow fixed at 32 L/min. The quality factor (QF) could be calculated by the following Eq. (1):

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

(1)

where \(\eta\) and \(\Delta P\) represented the filtration efficiency and pressure drop across the filter, respectively.

2.5. Antibacterial test

\(E. coli\) (ATCC 8739) and \(S. aureus\) (CMCC 26003) were utilized for antibacterial test. The ability to kill planktonic bacterium was tested as follows. PA6 ENM and PA6@Ag ENM were sterilized under UV for 2 h. \(E. coli\) and \(S. aureus\) were cultured for an overnight before. The sterilized membranes (3 cm × 3 cm in area) were put into NB broth with \(E. coli\) strains and TSB broth with \(S. aureus\) strains. The same initial concentration of bacteria suspension was as a blank control group. Then bacteria suspension was incubated at 37 °C, 200 rpm/min for 24 h with vibrating in thermostat oscillator. Bacterial growth curves of \(E. coli\) and \(S. aureus\) were determined by measuring OD at 600 nm by microplate reader (Bio-RAD 680, USA) at various contact times from 0 to 24 h.

In order to test the antibacterial property for adhered \(E. coli\) and \(S. aureus\), the sterilized ENMs (1 cm × 1 cm in area) were introduced into 12-well culture plate of 2 mL NB broth added 1% sucrose with \(E. coli\) and TSB broth added 1% sucrose with \(S. aureus\), followed incubation at 37 °C for 24 h in thermostat incubator to form biofilm. Then, a part of PA6 ENM and PA6@Ag ENM were washed by sterile PBS (0.01 mM, pH 7.3) to wash away the planktonic bacteria, with following addition of 2 mL 0.5 mg/mL MTT solution, incubation at 37 °C for 4 h, and gentle mix with 2 mL DMSO. After incubation, the solution was transferred to a new microtube and centrifuged at 4000 rpm for 10 min. The supernatant was placed in 96-well plate and the OD at 490 nm was tested by microplate reader (powerwaveXS2). After the fixation and dehydration step, the morphologies of bacterium on the other PA6 ENM and PA6@Ag ENM were visualized with SEM (Ultra Plus-43-13, Germany).

2.6. Antiviral test

The sterilized PA6@Ag ENM and PA6 ENM (circular membrane with diameter of 25 mm) were placed at the bottom of 12-well culture plate which already was added 1 mL PDCoV samples (MOI = 1.0). The time of interaction between the membrane and virus solution was 15 min, 30 min, and 60 min at 4 °C, then 100 μL PDCoV solution was extracted at each time point, and three samples were taken in parallel. The number of infectious PDCoV particles was determined on the basis of the 50% tissue culture infectious dose (TCID50) in swine testicular (ST) cells. 100 μL PDCoV solution was diluted by Dulbecco’s modified eagle medium (DMEM) with 1% Pancreatin and 0% serum. The ST cells seeded into 96-cell plates grown to 100% were infected using 10-fold serial dilutions of PDCoV. After incubation at 37 °C for 2 h, the cells were washed three times with PBS and incubated for 72 h. Through observed cell plates under an electron microscope, cytopathic effect (CPE) was monitored and counted that was frequently in inoculated ST cells. Titers are reported as TCID50 calculated by the method of Reed and Muench.

2.7. Cytotoxicity test

The relative growth rate and toxicity of cells were determined by MTT assay. PA6@Ag ENM and PA6 ENM were cut into 1 cm × 1 cm and sterilized by medical alcohol then showered by PBS. These membranes were in 12-well plates with MC3T3 cells, which were cultured in α-MEM containing 10% PBS and 1% streptomycin–penicillin and maintained under 5% CO₂ atmosphere at 37 °C. The cells were initially cultured for 48 h in growth culture medium. Then, membranes and culture medium were replaced by MTT. The cells were cultured for 2 h. The MTT solution in each well was replaced by DMSO. The absorbance of the solution was determined by measuring OD at 490 nm by microplate reader. The relative growth rate (RGR) could be calculated by the following Eq. (2):

\[
\text{RGR} = \frac{\text{OD}_{1} - \text{OD}_{0}}{\text{OD}_{1}} \times 100\% 
\]

(2)

where \(\text{OD}_{1}\) and \(\text{OD}_{0}\) represented OD values of experimental group and control group, respectively.

The cytotoxicity grade was assessed according to the cytotoxicity grading criteria shown in Table 1 (Sun et al., 2016).

2.8. Evaluation of capture property for gaseous pollutants in field test

In this study, air pollutants were generated by burning mosquito-repellent incense, since there were various gaseous pollutants in this smoke. In order to study the filter efficacy and gaseous pollutants removal of PA6@Ag ENM in real polluted air indoor, PA6@Ag ENM was installed on the air conditioner in one room. And as a control, the other

| Cytotoxicity grade | Cytotoxicity grade |
|-------------------|-------------------|
| 100+              | 0 (non-poisonous, qualification) |
| 75–99             | 1 (slightly poisonous, qualification) |
| 50–74             | 2 (moderately poisonous, qualification) |
| 25–49             | 3 (severely poisonous, qualification) |
| 1–24              | 4 (disqualification) |
| 0                 | 5 (disqualification) |
air conditioner didn’t do any treatment in an adjoining room with the same furniture. After burning out two cigarettes in every room, open the air conditioners immediately and the air conditioners temperature set at 20 °C. The concentration of PM2.5 indoor was began to measure in real time by PM2.5 detector (Bohua Kangsheng Technology Co., Ltd., China)). Until the concentration value was stable, the experiment was over.

2.9. Characterization

The crystal structure of Ag NPs, PA6 nanofibers, and PA6@Ag nanofibers was characterized by powder X-ray diffraction (XRD, Bruker D8 Advance diffractometer) using Cu Kα (λ = 1.5418 Å) radiation. The SEM images and EDX were taken by Field Emission Scanning Electron Microscopy (FE-SEM, Ultra Plus-43-13, Germany). The chemical structure of membrane was examined by Fourier transformation infrared spectrophotometer (FTIR, Thermo Nicolet, Nexus, in wavenumber range of 400–4000 cm⁻¹). The UV–vis spectra of PA6@Ag ENM and Ag NPs were collected using UV spectrometer (PerkinElmer Lambda 750S, USA). The basis weight is defined as the mass per unit area and usually measured in g/m². It was measured by an electronic balance with test area 10 cm × 10 cm. The corresponding content of Ag on PA6@Ag nanofibers was characterized by inductively coupled plasma-optical emission spectrum (ICP-OES, Leeman Labs Prodigy 7, USA). Tensile strength and elongation at break of electrospun membranes were tested using an electrical universal material testing machine (MTS Systems, China Co. Ltd) with the crosshead speed of 5 mm/min.

In order to test the stability of Ag NPs on nanofibers, two PA6@Ag ENMs were dipped into formic acid and deionized water with 20 min of shaking at 25 °C separately, then these liquids were tested by UV–vis spectra (PerkinElmer Lambda 750S, USA), TG analysis was conducted to test the silver content of total membranes under different pH values. At the end of impregnation process under different pH values, the pH value of as-prepared Ag NPs colloidal solution was 9. Fig. 1c shows that there is hardly any nanoparticle on the nanofiber surface, which means Ag NPs are not successfully immobilized on the nanofiber without acid treatment. With the addition of hydrochloric acid, the pH values of Ag NPs colloidal solution decreased gradually to 7, 5, 3. The corresponding morphologies of PA6@Ag ENM at different pH values are shown in Fig. 1d, e, f, respectively. Fig. 1d shows that there is a very small amount of nanoparticles randomly distributed on the nanofibers. As displayed in Fig. 1e, Ag NPs immobilize evenly on every fiber, forming bumpy nanorough structure, and corresponding SEM-EDS spectrum of Ag nanoparticles as shown in Fig. S2. It is clear in Fig. 1f that nanoparticles are more prone to conglomeration than immobilization on nanofibers, that influences the pores of membranes and goes against to filter efficiency and pressure drop. Fig. S3 shows the UV–vis spectroscopy of Ag NPs colloidal solution at the beginning and the end of impregnation process under different pH values. At the end of the impregnation process, Ag NPs were immobilized on the nanofiber, so the UV–vis spectroscopy of Ag NPs colloidal solution decreased.

Moreover, the inductively coupled plasma-optical emission was conducted to test the silver content of total membranes under different pH. With the addition of hydrochloric acid, the pH of Ag NPs colloidal solution decreased gradually and silver content was 0.06%, 0.23%, 1.18%, 4.29%, respectively. The result is consistent with morphology analysis. The sodium carboxylate groups on the citrate could be acidified becoming carboxylic acid groups, which could form hydrogen bond with amide of PA6. However, too much hydrochloric acid destroys the stabilizers of nanoparticles, leading to nanoparticles agglomerations. It is concluded that the optimum condition is pH 5 for assembling Ag NPs on PA6 nanofiber.

In Fig. 2a, FTIR analysis was applied to characterize possible interaction between PA6 and Ag NPs. In the FTIR spectrum of PA6 ENM, the typical adsorption peaks of 3302 cm⁻¹, 1308 cm⁻¹, 1645 cm⁻¹ and 1542 cm⁻¹ correspond to hydrogen-bonded N–H stretching, N–H Fermi resonance, amide I, and amide II, respectively (Lee et al., 2008). The amide I band are primarily due to the carbonyl stretching vibration and the amide II band are mainly attributable to CN stretching and NH

3. Results and discussion

3.1. Morphology and structure of ENMs

Through early exploration of electrospinning process, PA6 nanofibrous membrane was on the PP nonwoven substrate. There is an obvious double-layer membrane in Fig. 1a, and the lower layer is the PP non-woven fibrous membrane, the upper layer is the PA6 nanofibrous membrane. Magnification of PA6 nanofibers as shown in Fig. 1b, the electrospun membrane consists of uniform and continuous PA6 nanofibers with an average diameter 90 nm. PP nonwoven fiber with an average diameter 2.8 μm is shown in Fig. S1.

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In-plane bending. In the FTIR spectrum of PA6@Ag ENM, all of the typical adsorption peaks of PA6 can be clearly observed, but there are also some shifts. Hydrogen-bonded N—H stretching, N—H Fermi resonance peaks shifts from 3302 cm\(^{-1}\) and 3087 cm\(^{-1}\) to 3300 cm\(^{-1}\) and 3085 cm\(^{-1}\), respectively. And amide I and amide II bonds shifts from 1645 cm\(^{-1}\) and 1542 cm\(^{-1}\) to 1644 cm\(^{-1}\) and 1541 cm\(^{-1}\), respectively. Shifts on FTIR demonstrate hydrogen bonding between carboxyl group and amide group (Hirashima et al., 2005). In addition, there is no obvious new absorption peak in the FTIR spectrum of PA6@Ag ENM, demonstrating the existence of hydrogen bond rather than chemical interaction between PA6 and Ag nanoparticles.

XRD measurements were applied to investigate the polymorphism of the Ag and PA6 ENM, whether or not it retains the crystal form PA6@Ag ENM. In Fig. 2b, compared with the crystal structure of PA6 ENM, PA6@Ag ENM displays the same crystallization peaks. Another characteristic peaks of PA6@Ag ENM at 38.2°, 44.3°, 64.4° and 74.4° are indexed to the crystal planes (111), (200), (220) and (311) of Ag NPs, respectively. XPS was conducted to analyze the state of Ag NPs of PA6@Ag ENM. XPS patterns for the PA6@Ag ENM and PA6 ENM is shown in Fig. 2c and Fig. S4. In Fig. 2d two peaks are detected at 367.82 eV, 373.9 eV correspond to Ag 3d\(^{5/2}\) and Ag 3d\(^{3/2}\) binding energies, respectively. The splitting of the 3d doublet is 6.08 eV, indicating that Ag mainly exists in metallic state on PA6 nanofibers (Soliman et al., 2017). Therefore, the XPS results confirmed that Ag metallic nanoparticles on the PA6 nanofiber. The XRD patterns and the XPS all reflect that Ag NPs immobilizing on the PA6 nanofibers.

Furthermore, we studied the stability of nanoparticles on fibers. It is very important because circulation of released nanoparticles is harmful. In Fig. 3a, the spectrum of the diluted solution of Ag NPs shows an absorption band at 391 nm, which is attributed to the surface plasmon resonance band (SPR) of Ag NPs. The SPR of PA6@Ag ENM is broadened and red-shifted slightly to 398 nm because of closed interparticle distance.

![Figure 2](image1.png)  
**Fig. 2.** (a) FTIR spectra of PA6 ENM and PA6@Ag ENM; (b) XRD patterns of Ag NPs, PA6 ENM and PA6@Ag ENM; (c) XPS pattern for the PA6@Ag ENM in the range of 600–200 eV; (d) XPS pattern in the range of 380–360 eV.

![Figure 3](image2.png)  
**Fig. 3.** UV–vis spectroscopy of (a) PA6@Ag ENM and Ag NPs, (b) PA6@Ag ENMs in formic acid and deionized water.
PA6@Ag ENMs were shaking 20 min at 25 °C in formic acid and deionized water, respectively. PA6@Ag ENM was soluble in formic acid and Ag NPs were released in solution, so that the UV–vis spectroscopy shows an absorption band at 398 nm in Fig. 3b. UV–vis spectroscopy of PA6@Ag ENM in deionized water doesn’t show any absorption band, which confirms that Ag NPs are stable on PA6 nanofiber.

Through tensile tests, we can see clearly that tensile strength, elongation at the break, and the stress—strain curves of PA6 ENM and PA6@Ag ENM in Fig. 4. The results obtained from 5 trials were averaged and reported. Tensile strength of 2.83 ± 0.15 MPa and elongation at the break of 92.08 ± 3.25% for PA6@Ag ENM were improved in comparison to PA6 ENM possibly due to the effective reinforcement provided by Ag NPs in the polymer matrix and stronger hydrogen bonding force. One result of the stress—strain curves is shown in Fig. 4c, indicating that the initial stage of PA6 ENM and PA6@Ag ENM stress-strain curve is the elastic deformation region. After this stage, there is a gradual decrease in the slope of the curve right up to break, since fiber break age with few fibers slipping in the rupture zone of broken specimen (Patel and Kothari, 2001).

The effective specific surface area and pore structure of the membrane have a great influence on the filtration performance. So N2 adsorption and desorption was conducted to study the pore structure of the PA6@Ag ENM and PA6 ENM. It can be obtained from Fig. 5 membranes emerged a typical IV isotherm according to the IUPAC standard, indicating the feature of mesopores with pore diameter between 2 nm and 50 nm (Wang et al., 2015; Yang et al., 2020b). Brunauer-Emmett-Teller (BET) surface area of PA6@Ag ENM and PA6 ENM is 0.75 ± 0.01 m²/g and 0.40 ± 0.03 m²/g, respectively. The result of surface area suggests that Ag nanoparticles can increase the specific surface area of membrane. The result is also corresponding with that bumpy and nanorough structure of PA6@Ag ENM, as shown in Fig. 1b and e. It may be conductive to improve the interception and filtration of fine particles.

3.2. Air filter performance

To quantitatively characterize the air filter performance of PA6@Ag ENM, the filtration efficiency and pressure drop were investigated for the neutralized sodium chloride particles with size of 0.3 μm to 0.5 μm. Fig. 6a exhibits the filtration efficiency and pressure drop of PA6 ENM and PA6@Ag ENM with various basis weight, which is obtained under different electrospinning time. The filtration efficiency curves show an upward trend with increasing the basis weight. With the PM0.3–0.5 filtration efficiency of PA6@Ag ENM raising from 61.05% to 99.99%, the pressure drop goes from 26 Pa to 267 Pa. The PA6@Ag ENM also displays lower pressure drop than PA6 ENM.

Smaller fiber diameter is beneficial for improving filtration efficiency, however, the corresponding pressure drop is also increased. Therefore, the overall filtration performance of the air filter considering both efficiency and pressure drop is assessed by QF. Higher QF value generally means better integrated filtration performance. According to the Eq. (1), the calculated QF values of membranes at different basis weight are shown in Fig. 6b. Compared with PA6 ENM, the PA6@Ag ENM displays significantly higher QF values, and the highest QF value of PA6@Ag ENM is 0.13 Pa⁻¹. The filtration efficiency of the PA6 ENM and PA6@Ag ENM of the highest QF values for the sub-micron particles from 0.3 to 10 μm is further investigated, as shown in Fig. 6c. The PA6@Ag ENM exhibits high filtration efficiency of 99.99% and low pressure drop of 31 Pa for PM2.5. Moreover, the corresponding pressure drop is at fairly low level. Generally, lower pressure drop means more energy-saving and less adverse impact on equipment.

Then, compared with other air filter membranes, such as PAN, PA6, PA6/PVDF, PVA-PAA-SiO2, and so on, PA6@Ag ENM also exhibits very good filter performance, as shown in Table 2 and Fig. S5. These above-mentioned results all reveal the contribution of designed structure on promoting air filtration performance. Bumpy and nanorough surfaces provide highly effective specific surface area and cumulative volume of pores, which could create the non-slip and stagnation of aerosol particles on the surface of fibers leading to high efficiency and low pressure drop of air filter (Wang et al., 2014; Al-Attabi et al., 2019; Li et al., 2018).

3.3. Capture property of aerosol pollutants

In this study, the aerosol pollutants were generated by burning mosquito-repellent incense since there are various gaseous pollutants in this smoke. The morphology of the PA6 ENM and PA6@Ag ENM after capturing smoke pollutants of mosquito-repellent incense is investigated by SEM shown in Fig. 7a, b. As illustrated in Fig. 7a, the aerosol particles are coated along with PA6 nanofibers. As for PA6@Ag ENM shown in Fig. 7b, vast areas of PA6@Ag ENM are covered by smoke pollutants. Further, the particles matters tend to connect together and form large domains on the surface of PA6@Ag ENM. The morphology
difference implies that the Ag NPs on PA6@Ag ENM acted as additional barriers for capturing gaseous pollutants.

Then, PA6 ENM and PA6@Ag ENM were detected by TA-MS with heating from room temperature to 350 °C. Ion intensity curves are based on unique mass-to-charge ratio of captured specific gas, as shown in Fig. 7c–f. The captured gaseous pollutants could be released under certain temperature (Ahmad and Alshehri, 2012). The release of SO2 during pyrolysis and combustion shown in Fig. 7c is confirmed by a fragment with m/z 64 (SO2+). Similarly, Fig. 7d–f display the ion intensity curves of the NO− 3, NO3− and methylbenzene correspond to fragments at m/z 30, 46, and 106 respectively during gas release. Furthermore, GC–MS was utilized to analyze the non-volatile or persistent chemical component from room temperature to 350 °C. The detected organic components are over 20 genera, while typical six genera of components have relatively high content, which account for over 72% of the total dissolved gaseous, as shown in Fig. 7g and Fig. S6a. PA6@Ag ENM exhibits significantly stronger capture capacity of isoprocarb than PA6 ENM in terms of the adsorbed organic components. Isoprocarb, one of the most common carbamates insecticides, has been found to denature the protein, which may exert toxic effects on human beings and animals (Ni et al., 2008). TG curves of PA6@Ag ENM and PA6 ENM before and after capturing smoke pollution as shown in Fig. S6b and Fig. 7h. Original ENMs could keep thermal stability at room temperature to 350 °C. After capturing smoke pollution, it is concluded from TG curves that PA6@Ag ENM captured more smoke pollution than PA6 ENM. As a result, PA6@Ag ENM exhibits strong harmful and toxic pollutants-capturing ability, which is crucial for ensuring human health under air pollution.

In order to study the filter efficacy and air pollutants capture capacity of PA6@Ag ENM in real polluted air environment indoor, PA6@Ag ENMs are installed on the air conditioner. After burning two cigarettes in room, the concentration of PM2.5 indoor is up to ~400 μg/m3, and then the air conditioner is adjusted to 20 °C. The SEM image in Fig. 8a shows the morphology of nanofibrous filter after test. The PM particles of 0.2–3 μm in the air are captured by nanofibers. In Fig. 8b, with time going by, the concentration of PM2.5 in room with PA6@Ag ENM decreases faster than without one. According to ambient air quality standards of China, the concentration of PM2.5 in the air more than 75 μg/m3 means that air is polluted. The concentration of PM2.5 with ENM reduces to less than 75 μg/m3 for 4 h and remains at ~40 μg/m3 finally, which exhibits more excellent pollutants-capturing capacity. Fig. 8c displays the ion intensity curves of phenol corresponded to fragments at m/z 94. The GC–MS detection result is displayed in Fig. 8d. The detected main composition is nicotine, which content is 59.58%. As we all known, secondhand smoke is a big health hazard and nicotine is one of the main composition. Barn et al. reported that HEPA filter air cleaners can lower indoor PM2.5 concentrations and second hand smoke exposures in highly polluted settings (Barn et al., 2018). These experimental results also demonstrate that PA6@Ag ENM installed on air conditioning can effectively capture dangerous cigarette smoke composition in the air, rather than simply block it. This membrane is effective to protect people from the dangers of aerosol pollutants.

### 3.4. Antibacterial performance

In order to study the antibacterial performance of the as-prepared air filters, PA6@Ag ENM was assessed against *E. coli* (Gram-negative bacteria) and *S. aureus* (Gram-positive bacteria). Fig. 9a shows the effects of PA6@Ag ENM on bacterial growth of *E. coli* in NB-broth. The time dependent growth of *E. coli* has been studied by measuring the optical density (OD) at 600 nm. The OD value shows typical growth curve of *E. coli* for PA6 ENM control group, but the OD value shows obvious decrease for PA6@Ag ENM group. Similarly, Fig. 9e shows the effects of PA6@Ag ENM on bacterial growth of *S. aureus* in TSB-broth. It indicates that Ag NPs on PA6@Ag ENM lead to inhibition of bacteria growth curves, which means that PA6@Ag ENM exhibits excellent antibacterial ability to planktonic *E. coli* and *S. aureus*.

To further study the antibacterial ability to adhered bacteria, *E. coli* and *S. aureus* in stationary phase was grown on ENMs. The MITT cell metabolism assay of *E. coli* and *S. aureus* were shown in Fig. 9b, f.

### Table 2

The filtration performances of different membranes.

| Samples         | Filtration efficiency (%) | Pressure drop (Pa) | Quality factor (Pa⁻¹) | Face velocity (μm/s) | Particle material | Reference     |
|-----------------|---------------------------|-------------------|-----------------------|----------------------|------------------|--------------|
| PAN             | 96.12                     | 133               | 0.024                 | 0.21                 | PM2.5            | Liu et al., 2015 |
| PA6             | 99.56                     | 270               | 0.020                 | 0.2                  | PM2.5            | Xu et al., 2016  |
| PVA/PAA/SiO2-Ag| 95.34                     | 90                | 0.0339                | 32 L/min             | PM2.5            | Zhu et al., 2018 |
| BaTiO3@PU/PSA   | 97.36                     | 24.1              | 0.151                 | 2 m/s                | PM2.5            | Yang et al., 2020b |
| PA6@Ag          | 99.99                     | 31                | 0.3                   | 32 L/min             | PM2.5            | This work      |
| PA6-PAN         | 99.99                     | 80                | 0.1163                | 90 L/min             | PM2.5            | Wang et al., 2015 |
| PA6/PMIA        | 99.995                    | 101               | 0.1                   | 32 L/min             | PM2.5            | Zhang et al., 2016 |
| PAN/β-CD        | 95.5                      | 112               | 0.027                 | 0.06 m/s             | PM2.5            | Kadam et al., 2018 |
| PAN/BaTiO3      | 98.6                      | 68.13             | 0.05                  | 0.03 m/s             | PM2.5            | Bortolussi et al., 2019 |
| PVP/PAN/PS      | 99.96                     | 54                | 0.1449                | 0.053 m/s            | PM2.5            | Cai et al., 2020  |
| PA6@Ag          | 97.98                     | 31                | 0.13                  | 32 L/min             | PM2.5            | This work      |
from PA6@Ag ENM all exhibit significantly lower metabolic activity than those from the PA6 ENM. In addition, the morphologies of E. coli and S. aureus on ENMs were measured by SEM. Fig. 9c shows the typical rod-like morphology of E. coli grown on PA6 ENM, rather than cell-lysis of E. coli phenomenon on PA6@Ag ENM in Fig. 9d. Similarly, the morphology of S. aureus was uniform spherical shape with smooth surface on PA6 ENM in Fig. 9g. However, Fig. 9h shows that the cell membranes of S. aureus were broken, pitted and shriveled, with grainy and rough surface. Ag NPs bonded on the PA6@Ag ENM probably destroy the cell integrity by damaging the cell membrane, resulting in the death of bacteria (Liao et al., 2019). In conclusion, PA6@Ag ENM exhibits excellent antibacterial property.

3.5. Cytotoxicity in vitro

MC3T3 cells are mouse osteoblasts, widely used as model systems on the biology of osteoblasts in oral surgery and medicine (Takechi et al., 2016; Deana et al., 2018). Gaseous pollutants often penetrate into human organs first through respiratory system. The cytotoxicity of PA6@Ag ENM to MC3T3 cells was studied in this paper. The viability
of MC3T3 cell in various groups was tested through the MTT assay. Fig. 10 shows OD values of the blank control group, PA6 ENM and PA6@Ag ENM measured by MTT assay after 48 h of incubation, and the relative growth rate (RGR) calculated by OD values using the Eq. (2). RGR of PA6 ENM and PA6@Ag ENM were 97.36% and 99.07%, respectively, and the grade of cytotoxicity was level 1-slightly poisonous (75–99%) in Table 1. Recently, it is reported the dose, time, and size dependency of the Ag-NPs mediated cytotoxicity (Liao et al., 2019; Salem et al., 2020). The result indicates that PA6@Ag ENM has little hazardous effect on cell proliferation.

3.6. Virus inhibition

PDCoV is a positive-sense RNA virus, with typical morphology of Coronaviruses (Zhang, 2016). Here, the antiviral assay of PA6@Ag ENM against to PDCoV was studied. To illustrate the effect of PA6@Ag ENM on PDCoV, ENMs were contacted with PDCoV at different times. PA6 ENM was a control group. Compared with PA6 ENM, the viral contents have no significant reduction treated with PA6@Ag ENM at 15 min. But they significantly decrease in ST cells at 30 min, and continue to decline at 60 min in Fig. 11. Therefore, we can conclude that PA6@Ag ENM exhibits obvious antiviral effects PDCoV due to Ag NPs.

4. Conclusion

The as-prepared PA6@Ag ENM has been constructed with fine diameter, high specific surface area and bumpy nanorough structure. In summary, we presented an efficient method to prepare PA6@Ag ENM, which shows high PM2.5 filtration efficiency, low pressure drop, and high removal performance of gaseous pollutants and remarkable antibacterial property, antiviral property and not significant cytotoxicity. The membranes fixed on the air conditioner also show excellent air purification performance in a field test. We believe that multifunctional membrane with bumpy nanorough structure could be served as effective air filter membrane applied to more devices to against infectious agents and protect human health.

CRediT authorship contribution statement

Yanyun Ju: Validation, Investigation, Writing – original draft, Writing – review & editing. Ting Han: Visualization. Jiajun Yin: Methodology. Qianqian Li: Methodology. Zhuo Chen: Investigation. Zhanyong
Wei: Supervision. Yang Zhang: Supervision. Lijie Dong: Conceptualization, Supervision, Project administration.

Declaration of competing interest
The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

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Appendix A. Supplementary data
Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2021.445768.

References
Ahmad, T., Alshehri, S.M., 2012. TG-FITR-MS (evolved gas analysis) of bidi tobacco powder during combustion and pyrolysis. J. Hazard. Mater. 199, 200–208.
Althairi, M.R., Ricketts, W., Fortheringham, T., 2020. Use of an antiviral filter attached to a pleural drain bottle to prevent aerosol contamination with SARS-CoV-2. Clin. Med. (Lond). 20, E60–E61.
Al-Attabi, R., Morsi, Y., Kujawski, W., Kong, L., Schütz, J.A., Dumée, L.F., 2019. Wrinkled silicic doped electrospun nanofiber membranes with engineered roughness for advanced aerosol air filtration. Sep. Purif. Technol. 215, 500–507.
Anderson, J.O., Thundiyil, J.G., Stolbach, A., 2012. Clearing the air: a review of the effects of enhanced aerosol air. Filtration. Sep. Purif. Technol. 215, 500–507.
Ahamad, T., Alshehri, S.M., 2012. TG-FTIR-MS (evolved gas analysis) of bidi tobacco powder during combustion and pyrolysis. J. Hazard. Mater. 199, 200–208.
Althairi, M.R., Ricketts, W., Fortheringham, T., 2020. Use of an antiviral filter attached to a pleural drain bottle to prevent aerosol contamination with SARS-CoV-2. Clin. Med. (Lond). 20, E60–E61.
Ahamad, T., Alshehri, S.M., 2012. TG-FTIR-MS (evolved gas analysis) of bidi tobacco powder during combustion and pyrolysis. J. Hazard. Mater. 199, 200–208.

Yang, L., Li, C., Tang, X., 2020a. The impact of PM2.5 on the host defense of respiratory system. Front. Cell. Dev. Biol. 8, 91.
Yang, L., Li, C., Tang, X., 2020b. The impact of PM2.5 on the host defense of respiratory system. Front. Cell. Dev. Biol. 8, 91.

Yang, L., Li, C., Tang, X., 2020a. The impact of PM2.5 on the host defense of respiratory system. Front. Cell. Dev. Biol. 8, 91.
Yang, L., Li, C., Tang, X., 2020b. The impact of PM2.5 on the host defense of respiratory system. Front. Cell. Dev. Biol. 8, 91.