Green electrospun and crosslinked poly(vinyl alcohol)/poly(acrylic acid) composite membranes for antibacterial effective air filtration

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Abstract

Air pollution has become a major environmental concern given the ever increasing levels of particulate matter (PM) and the increased in treatment-resistant bacterial and viral strains. Major efforts are therefore required into the development of air filtration and purification technology as well as novel, alternative antiviral and antibacterial treatment modalities. Here, we report an environmentally friendly method for the generation of multifunctional poly(vinyl alcohol)/poly(acrylic acid) (PVA-PAA) composite membranes via green electrospinning and thermal crosslinking. Superhydrophobic silica nanoparticles were then incorporated into the fibers resulting in a rough surface, after which AgNO₃ was introduced, resulting in the formation of Ag nanoparticles through UV reduction. The PVA-PAA-SiO₂-Ag NPs membranes were found to possess high air filtration performance (with >98% filtration efficiency for PM₂.₅) as well as potent antibacterial and antiviral activities. The green synthesis approach avoids the use of hazardous organic solvents, thereby bypassing any potential toxicity concerns caused by organic solvent residues. These newly designed PVA-PAA-SiO₂ NPs-Ag NPs nanofibrous membranes with many superior features
1. Introduction

Over the past decades, the loss of air quality has become one of the most serious environmental issues and poses significant threats to human health [1,2]. One of the main causes of air pollution lies in the ever-increasing presence of particulate matter (PM), which is a complex mixture of liquid droplets and small particles that can be made up of either inorganic (e.g., silicates, sulfates, and nitrates) and organic matter (e.g., organic carbon and elemental carbon) [3,4]. The increase in PM levels is a global problem, instigated by the rapid industrialization in several newly developed countries (e.g., India and China), where in large parts of the countries the level of PM continuously exceeds the highest US environmental protection agency (EPA) threshold (“hazardous”, greater than 250 μg/m³) [5,6]. This has resulted in the recording of millions of deaths in China per annum due to vehicular and industrial emissions [7,8], along with the highest premature mortality of 1.36 million deaths every year [9,10]. Among the airborne fine particle pollutants, especially those with an aerodynamic diameter smaller than 2.5 μm (PM2.5), have been proven to be a primary cause of adverse health problems [11] including chronic lung disease, cancer and fibrosis [12]. Up to present, improvements in air quality can be realized either via reducing the emission of PM or via air filtration [13]. The latter is the only option available for personal protection, resulting in a strong need for high performance air filtration media [14].

Air filtration is the most promising [12] and effective approach to purify air at low costs [15]. Technically speaking, conventional filtration media typically consist of micrometer-scale fibers, such as glass fibers or melt-blown fibers [14] that are incapable of capturing fine particles [11] because the pore sizes formed with micro-sized fibers are fairly large, and their performance for capturing PM2.5 is still far from satisfactory [16]. On the contrary, electrospun nanofibrous membranes display excellent filtration performances (high filtration efficiency, low pressure drop) compared with traditional air filtration membranes due to their remarkable surface area to volume ratio, high porosity, interconnected pore structure and controllable fiber diameter [17,18]. Theoretically, nanofibers with diameters less than 500 nm [19] would boost the filtration efficiency [1] by the so-called enhanced “slip effect” [14], which is beneficial for simultaneous low airflow resistance [19]. Benefitting from this feature of electrospun nanofibrous membranes, an increasing research effort has been committed to develop electrospun air filters. For this purpose, many polymer materials, such as polycrylonitrile (PAN) [2], polyurethane (PU) [11], polyamide-66 (PA-66) [20], polyimide (PI) [6,21], polyamide-56 [22], polysulfone [23], have been successfully used to produce efficient air filtration membranes [22]. However, big challenges remain concerning the preparation of multifunctional, high-performance air filtration membranes [19], using an environmentally friendly synthesis method enabling both filtration of PM from air as well as filter out and deactivate bacteria and viruses. The latter is generally considered as the second main hazard concerning air pollution as next to PM pollutants in the atmosphere also include microorganisms such as bacteria and viruses, that may cause respiratory infectious diseases or allergies [24]. The increase in antibiotic resistant bacterial strains and the emergence of resistant viral strains stress the need for the development of safe and potent alternatives to conventional antiviral drugs [25]. One recently introduced promising alternative are nanoparticles (NPs), and in particular silver NPs, which have been proven to possess potent antibacterial and antiviral properties [26]. As the process of electrospinning enables the incorporation of NPs into the polymer matrix [26], this can be exploited to achieve multifunctional performances (i.e. air filtration from PM and antibacterial/antiviral efficacy).

In existing air filtration membranes, not much work has been devoted on the development of “environmentally friendly” synthesis procedures for the generation of filter membranes that would be safe for continuous use by individuals for prolonged time periods. Most of the polymers used (such as those mentioned above) to prepare air filtration membranes are dissolved in organic solvents, which means the fabrication process involves the use of harmful to highly hazardous solvents [27]. Those residual organic solvents might be flammable [28] and toxic to both humans and the environment, [29]. Exposure to these solvents, either at high concentrations during manufacture or research in the laboratory, or prolonged exposure at low concentrations in the final product may elicit environmental and human harm [27]. This promotes the generation of "green electrospinning" technology [27,30], which could be defined as an approach which would alleviate concerns regarding safety, environmental problems and toxicology [31], through the fabrication of electrospun fibers based on aqueous polymer solutions [27]. One main impediment to the use of “green electrospun fibers” is that they would be unstable in an aqueous environment [27]. This can be overcome through crosslinking technology (by either physical or chemical means). However, many chemical crosslinkers, such as glutaraldehyde, are also toxic [32] rendering physical crosslinking approaches to be the optimal choice for a full green electrospinning approach.

Here, we explore the application of poly(vinyl alcohol)/poly(acrylic acid) (PVA-PAA) nanofiber membranes which were fabricated via green electrospinning and thermal crosslinking. Furthermore, we will aim to incorporate hydrophobic silica (SiO₂) NPs into the PVA-PAA nanofiber membranes, in order to create a hierarchical roughness on the nanofiber surfaces and hereby enhance the filtration performance. The hydrophobic silica NPs not only contribute to the hierarchical structure of the filters but also endowed pristine membranes with promising self-cleaning performance [33]. To achieve multifunctional air filtration membranes, silver nitrate (AgNO₃) was doped into the PVA-PAA- SiO₂ NPs filtration membranes and reduction of Ag⁺ to Ag nanoparticles (Ag NPs), was performed via UV reduction, to bestow the membranes with potent antibacterial/antiviral activity. PVA-PAA-SiO₂-Ag NPs nanofibrous membranes (Scheme 1(a) and (b)) will then be tested regarding their air filtration efficacy both in view of filtering out PM, in particular PM2.5, and in achieving efficient antibacterial/antiviral efficacy.

2. Experimental section

2.1. Materials

Poly(vinyl alcohol) (PVA-124, 98–99.8% hydrolyzed), agar powder and beef extract were purchased from Sinopharm Chemical Reagent Co., Ltd. China. Poly(acrylic acid) (PAA, 50% aqueous solution, Mw ~ 50,000) was purchased from Shanghai Macklin Biochemical Co., Ltd. Hydrophobic silica nanoparticles (SiO₂ NPs,
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Preparation of PVA-PAA nanofibrous membranes

Solutions of 10 wt% PVA were prepared by dissolving 4 g of PVA in 36 ml of ultra-pure water and incubated at 80 °C for 4 h, after which the PVA solution was allowed to cool to room temperature. A blend solution of PVA/PAA was made by mixing the aqueous polymer solutions in different molar ratios (–OH/–COOH: 10/1, 5/1, 1/1, 1/5, 1/10) with a magnetic stirrer for 3 h at room temperature.

Electrospinning of PVA-PAA nanofibers: The aqueous polymer mixture was placed into a syringe with a blunt ended metallic needle with 0.7 mm inner diameter. All the nanofibrous membranes were spun at 17 kV keeping a constant tip-to-collector distance of 12 cm, and a solution flow rate of 0.66 ml/h. The electrospinning chamber was kept at constant temperature (25 °C) and relative humidity (45%). The electrospun PVA-PAA nanofibers membranes were carefully detached from the collector and thermally crosslinked at 140 °C for 2 h to induce esterification (Scheme 1 (c)).

Preparation of PVA-PAA-SiO2 NPs electrospinning solution: A blend solution of PVA-PAA (mole ratio: 1/1) was diluted by using ultra-pure water (1.5 g). Additionally, PVA-PAA solution containing 2, 4, 6 and 8 wt% of SiO2 NPs (relative to the PVA-PAA electrospun solution) which was wetted by ethanol (1 g), respectively, was prepared. Then the electrospinning solution was mixed with a magnetic stirrer for 3 h at room temperature followed by ultrasonication for 1 h to form a homogeneous solution.

Electrospinning of PVA-PAA-SiO2 NPs nanofibers: The nanofibrous membranes were fabricated using commercially available electrospinning equipment (FM1206, Beijing Future Material Sci-tech Co., Ltd., China). Before electrospinning, a nanowoven substrate (15 cm x 15 cm) was mounted on the fiber collecting drum (12 cm in diameter) at a drum rotation rate of 50 rpm. Typically, the homogeneous solution was injected through a metal needle with a controllable feed rate of 0.66 ml/h for electrospinning under a high voltage of 17 kV and keeping a constant tip-to-collector distance of 12 cm. To guarantee the uniformity of nanofiber membranes, the injection pump horizontally moved forward and backward at a speed of 0.3 mm/s with a 20 mm distance by using the mechanical slide unit. To stabilize the electrospun nanofiber membranes, the PVA-PAA-SiO2 NPs nanofiber membranes were dried in vacuum for 1 h (60 °C) to evaporate any residual ethanol and ultra-pure water after which they were thermally crosslinked at 140 °C for 2 h.

Preparation of PVA-PAA-SiO2-Ag NPs electrospinning solution: For the preparation of Ag NPs-doped membranes, a AgNO3 doped electrospun solution was used, which was fabricated by...
dissolving 0.1, 0.2, 0.3, 0.4 and 0.5 wt% AgNO₃ (relative to PVA-PAA electrospun solution) into PVA-PAA-SiO₂ NPs (4 wt%) solution, respectively. Then the electrospinning solution was mixed with a magnetic stirrer for 3 h at room temperature followed by ultrasonication for 1 h to form a homogeneous solution.

**Electrospinning of PVA-PAA-SiO₂-Ag NPs nanofibers:** The fabrication of hybrid PVA-PAA-SiO₂ NPs-Ag NPs nanofibers that were deposited on the nonwoven substrate which covered the grounded collector, being a rotating collecting drum at a rotation rate of 50 rpm. All the nanofibrous membranes were spun at 17 kV keeping a constant tip-to-collector distance of 12 cm. The feeding rate of the electrospun solutions by the syringe pump was 0.66 ml/h. To guarantee the uniformity of the thickness and base weights of the nanofibrous membranes, the injection pump horizontally moved forward and backward at a speed of 0.3 mm/s with a 20 mm distance by using the mechanical slide unit. The thickness and base weights of the membranes was controlled by varying the spinning duration. The residual solvents (ethyl alcohol and ultra-pure water) were removed by heating the membranes for 1 h (60 °C) in vacuum after which the fibers were thermally crosslinked at 140 °C for 2 h.

**Reduction of Ag⁺ ions:** After heat treatment, the PVA-PAA-SiO₂-Ag NPs nanofibrous membranes were treated under ultraviolet (UV) lamp (254 nm, 20 W) for six hour to allow UV reduction of the Ag⁺ ions to form Ag NPs.

**Preparation of PAN (polyacrylonitrile)-SiO₂ NPs-Ag NPs nanofibrous membranes**

**Preparation of PAN-SiO₂ NPs-Ag NPs electrospinning solution:** For the preparation of Ag NPs-doped membranes, a AgNO₃ doped electrospun solution was used, which was fabricated by dissolving 0.3 wt% AgNO₃ (relative to PAN electrospun solution) and SiO₂ NPs (4 wt%) into 15 wt% PAN solution which dissolved in DMF (N,N-Dimethylformamide, organic solvent). Then the mixed electrospun solution with a magnetic stirrer for 3 h in room temperature and ultrasound for 1 h to form a homogeneous solution.

**Electrospinning of PAN-SiO₂ NPs-Ag NPs nanofibers**

The fabrication of hybrid PAN-SiO₂ NPs-Ag NPs nanofibers that were deposited on the grounded collector, being a rotating collecting drum at a rotation rate of 50 rpm. The nanofibrous membranes were spun at 17 kV keeping a constant tip-to-collector distance of 12 cm. The feeding rate of the electrospun solutions by the syringe pump was 0.66 ml/h. The residual organic solvents (DMF) of PAN-SiO₂ NPs-Ag NPs nanofibers were removed by heating the membranes for 1 h (60 °C) in vacuum. The residual organic solvents of PAN₂-SiO₂ NPs-Ag NPs nanofibrous membranes without any treatment.

**Reduction of Ag⁺ ions:** The PAN-SiO₂ NPs-Ag NPs nanofibrous membranes were treated under ultraviolet (UV) lamp (254 nm, 20 W) for six hour to allow UV reduction of the Ag⁺ ions to form Ag NPs.

**2.6. Characterization of electrospun fibers**

The morphology of relevant membranes was performed using a field emission scanning electron microscope (FE-SEM, S-4800, Hitachi Ltd., Japan). Fourier transform infrared (FT-IR) spectra were recorded with a Nicolet 8700 FT-IR spectrometer. TEM images were captured with a JEM-2100 (Japan) transmission electron microscope. The acceleration voltage was 100 kV. The mechanical properties of the membranes were evaluated on an electronic universal testing machine (UTM6502, Shenzhen Sans Technology Stock Co., Ltd., China). Thermogravimetric analysis was performed using Thermal Gravimetric Analyzer (TGA Q5000-IR, TA Instruments). The optical microscope photographs were recorded with a Fluorescence microscope (OLYMPUS-IX 53, Japan).

**2.7. The hydrolysis experiments**

To investigate the hydrolysis performance of crosslinked PVA-PAA membranes with different molar ratios, the cross-linked PVA-PAA membranes with different molar ratios were immersed in ultra-pure water at room temptation for 24 h. Then dry in vacuum oven for 3 h (100 °C), and the change of surface morphology was observed by SEM.

Furthermore, the PVA-PAA membranes with different molar ratios were immersed in boiling water for 3 h, and the rate of weight loss was calculated according to formula (1).

\[
W = \frac{M_1 - M_2}{M_1} \times 100\% 
\]  

where \(M_1\) is the weight of thermally crosslinked PVA-PAA nanofibrous membranes before boiling, \(M_2\) is the weight of thermally crosslinked PVA-PAA nanofibrous membranes after boiling and drying.

**2.8. Thermal and mechanical properties**

The thermal stability of the green electrospun nanofiber membranes was performed using thermal gravimetric analysis from 30 °C to 800 °C in nitrogen atmosphere and the temperature programming is 10 °C/min. The tensile tests were carried out by a universal tensile tester, equipped with a load cell which has a maximum load of 50 N with a resolution of 0.001 N. Note that the average thickness of the green nanofibrous membranes samples (0.5 cm × 4 cm) were measured using a digital micrometer (Measured proof, Germany), and the membranes were stretched at a speed of 5 mm/min while the gauge length is set to 25 mm.

**2.9. Air filtration performance of membranes**

To measure the air filtration performance of the membranes, the green electrospun membranes with 100 cm² of effective area were put on a filter holder. The tester could deliver charge neutralized monodisperse solid NaCl aerosol particles and DEHS aerosol particles that had a mass mean diameter of 300–500 nm. The neutralized NaCl aerosol particles or DEHS aerosol particles were fed into a filter holder (upstream) and down through (downstream) the green electrospun membranes. The filter air flow resistance was measured with the combination of a flow meter and two electronic pressure transducers that detected the pressure drop through the filtration medium under testing. The test was conducted at a flow rate of about 32 L/min. All the nanofiber membranes were tested three times.

**2.10. Zone of inhibition test**

First, the nutrient agar was poured onto the disposable sterile Petri dishes and was allowed to solidify. For the qualitative evaluation, suspensions of *E. coli* and *S. aureus* (0.5 mL each) were spread onto agar plates uniformly. The membranes were cut evenly, resulting in circular membranes of 6 mm diameter. The samples of Ag NPs doped membranes and control samples (PVA-PAA-SiO₂ NPs membranes) were placed gently over the solidified agar plate and were spaced out in the petridish. The plate was incubated at 37 °C for 18 h. The antibacterial activity was identified and estimated by a clear zone of bacterial inhibition. The size of the clear zone was then quantified using ImageJ. These tests were conducted in three independent repeats.

**2.11. Cytotoxic activity**

**Cell culture:** L929 cells were routinely cultured in Dulbecco's modified Eagle's medium (DMEM, Nanjing, China) supplemented
with 10% fetal bovine serum (FBS) and cultured at 37 °C in a humid atmosphere with addition of 5% CO2. When the confluence reached 80% the cells were passaged. Cell culture media were removed and fresh media were given three times a week.

**In vitro cytotoxicity test:** Either green synthesized PVA-PAA-SiO2-Ag NPs nanoparticles or PAN1 (polyacrylonitrile)-SiO2 NPs-Ag NPs nanofibers (with heat treatment to removal of organic solvents) and PAN1-SiO2 NPs-Ag NPs nanofibers (without any treatment) (1.5 cm × 1.5 cm) synthesized in organic solvent were placed on the bottom of sterile 6 well plates, respectively. After this, the cells were added which were seeded at a density of 4 × 10^4 cells/well and incubated for 24 h. Following the exposure, the cells were treated with Trypan blue (HeFei BoMei Biotechnology Co. Ltd), to differentiate between live and dead cells. Cells were then viewed under an optical microscope (OLYMPUS-IX 53, Japan).

**L929 seeding efficiency:** The efficiency of L929 seeding on electrospun nanofibrous membranes (PVA-PAA-SiO2 NPs-Ag NPs nanofibers membranes, PAN1-SiO2 NPs-Ag NPs nanofibers membranes and PAN2-SiO2 NPs-Ag NPs nanofibers membranes) was quantified using MTT assay. To do that, we used DMEM medium to make extracts from the different membranes (1 mL DMEM was used to extract 3 cm² fibrous membranes). And the membranes were submerged into DMEM for 24 h (there are three parallel samples in each membranes to avoid errors). After centrifugation, the supernatant extract was filtered using 0.22 μm filters. The cells were treated with (diluted) extracts at 37 °C for 24 h. After incubating the cells with the extract, the extract was removed and the cells were washed twice with PBS. And then the fresh medium containing MTT solution (5 mg/ml in PBS) was added to the cells and incubated at 37 °C and 5% CO2. Four hours later, the medium was removed and 150 μL of DMSO solution was added to the cultures on a shaker for 10 min in order to dissolve the formazan crystals. Finally, the absorbance was measured with a microplate reader at 570 nm. The percentage of viability of the L929 cells were then calculated by comparison with untreated cells representing 100% viability (relative growth rate, RGR). The RGR was defined as:

\[
\text{RGR} = \frac{A_e}{A_0} \times 100\%.
\]

\(A_e\) being the absorbance measured in the experimental groups, \(A_0\) being the absorbance measured in case DMEM medium was used.

### 3. Results and discussion

#### 3.1. The hydrolysis-resistant performance of PVA-PAA nanofibrous membranes

PVA is a polymer that is commonly applied for the generation of air filtration membranes [34], due to its physical properties [35], thermal stability [36], excellent chemical resistance [35], low toxicity [36] and complete biodegradability [35]. A major drawback however, is that PVA membranes will dissolve immediately upon contact with water [37]. To overcome this drawback, one can exploit the high degree of functionality of the PVA polymer (a poly-hydroxy polymer [35]), which allows several chemical and physical methods to modify the polymer [37]. To render the PVA membranes water-insoluble, one promising way is crosslinking of PVA via heat-induced esterification with PAA [37,38]. Additionally, PAA can be used for air filtration membranes as well [39].

To investigate the hydrolysis stability of the PVA-PAA nanofibrous membranes, the electrospun PVA-PAA blend nanofiber membranes (stabilized with heat treatment) with different molar ratios (−OH:−COOH) were immersed in ultra-pure water for 24 h and then dried before analysis by scanning electron microscopy (SEM). With the increase of PAA content, the hydrolysis-resistant performance of PVA-PAA nanofibrous membranes was first enhanced, and then weakened. Fig. 1(a–e) shows representative images of PVA-PAA nanofibrous membranes (different molar ratio of hydroxyl and carboxyl) which were immersed in ultra-pure water for 24 h. From the images, it can be observed that the PVA-PAA-c nanofibrous membranes (−OH:−COOH molar ratio = 1:1) best maintain their original morphology after exposure to water for 24 h (Fig. 1(c)). Compared to the PVA-PAA-c nanofibrous membranes, all other membranes with different PVA-PAA ratios were lost after being immersed in water after 24 h (Fig. 1(a, b, d, e)), displaying certain levels of disintegration (Fig. 15). These findings were confirmed by weighing fibers prior to and after exposure to water at 90 °C for 2 h, in order to accelerate the dissolution process (Table 1S). Corresponding SEM images (Fig. 25) further confirmed the stability of thermally crosslinked PVA-PAA-c nanofibrous membranes (−OH:−COOH molar ratio = 1:1) after having been exposed to 90 °C water for 2 h. Based on their high stability against hydrolysis, PVA-PAA-c (−OH:−COOH molar ratio = 1:1) nanofibrous membranes were chosen as the optimal system for further use.

The thermal crosslinking between PVA and PAA occurred through esterification between hydroxyl in PVA and carboxyl in PAA during heat treatment [40]. Fig. 2 show the FT-IR spectrum of thermally crosslinked PVA-PAA-c nanofibrous membranes (Fig. 2, red line) and PVA-PAA-c nanofibrous membranes without crosslinking (Fig. 2, blue line). The FT-IR spectrum of PVA-PAA-c nanofibrous membranes without crosslinking shows a large amount of hydroxyl groups (relative area of the −OH groups absorption at 3400 cm⁻¹). It also can clearly be seen that the stretching vibration of “−C=O” (1640 cm⁻¹) becomes stronger after thermal crosslinking, which means that the “−C=O” stretching vibration (1720 cm⁻¹) is normally shifted to the right through esterification between hydroxyl in PVA and carboxyl in PAA. The stability of the crosslinked PVA-PAA-c nanofibrous membranes, could furthermore be confirmed through simple testing, where the PVA-PAA-c nanofibrous membranes without crosslinking disintegrated immediately when it was submerged in water (90 °C, Fig. 3(a–c)), while the crosslinked PVA-PAA-c nanofibrous membranes were stable throughout (Fig. 3(d–f)).

#### 3.2. Filtration performances of PVA-PAA-SiO2 NPs nanofibrous membranes

In order to boost the air filtration performance of the PVA-PAA nanofibrous membranes, we introduced hydrophobic silica nanoparticles (SiO2 NPs) in the PVA-PAA blend solution, which created a multilevel structure of the PVA-PAA nanofibrous membranes. The SiO2 NPs increase the surface roughness [18] and as such significantly increase the effective surface area of the electrospun nanofiber membranes. Due to this, the introduction of moderate amounts of SiO2 NPs can enhance the filtration performance of nanofibrous membranes owing to the formation of a hierarchical structure [41]. To comprehend the role of SiO2 NPs (which creates the protrusion structure[18]) in improving the filtration performance of electrospun nanofibrous membranes, the filtration performance of the PVA-PAA-SiO2 NPs nanofibrous membranes (with the same basis weight of ~2.55 g/m²) containing various concentrations of SiO2 NPs were systematically investigated by using charge neutralized sodium chloride (NaCl) aerosol particles and diisooctyl sebacate (DEHS) oil aerosol particles in the size range of 300–500 nm under a standard airflow speed of 32 L/min, respectively. The NaCl aerosol particles are representative of inorganic matter, while DEHS particles represent organic matter and are frequently used model systems for air filtration studies [41,42]. As demonstrated in Fig. 4(a), the filtration properties of hierarchically structured PVA-PAA-SiO2 NPs nanofibrous membranes are clearly different than those of pure PVA-PAA...
nanofibrous membranes. Interestingly, the filtration efficiency and pressure drop of PVA-PAA-SiO$_2$ NPs membranes obtained with a varying content of SiO$_2$ NPs (0 wt%, 2 wt%, 4 wt%, 6 wt% and 8 wt %) displayed a clear influence on the level of SiO$_2$ NP dopant into the PVA-PAA polymer matrix for both NaCl (Fig. 4(a) and DEHS particles (Fig. 4(c)). For both particle types, the filtration efficiency (the red line) of PVA-PAA-SiO$_2$ NPs membranes reached a maximum of 78.1722% (NaCl) and 78.80027% (DEHS) at 4 wt% SiO$_2$ NPs doping.

To understand this maximum at 4% SiO$_2$ NPs doping, the effect of SiO$_2$ NP doping on fiber morphology was investigated using SEM. Fig. 5(a–e) displays representative SEM images of PVA-PAA-SiO$_2$ NPs membranes which contains different levels of SiO$_2$ NPs, revealing a clear hierarchical structure which is most prominent at higher SiO$_2$ NP contents. Upon comparing the different PVA-PAA-SiO$_2$ NPs membranes, the diameter size and diameter distribution of 4% SiO$_2$ PVA-PAA-SiO$_2$ NPs membranes were found to be smallest and narrower than for any other formulation (It may be more suitable for electrospinning when the silica content is 4 wt%), which led to the high filtration efficiency at the same base weight. The maximum filtration properties of membranes with 4% SiO$_2$ NPs could be attributed to the decreasing size of average fiber diameter (Fig. 5(c)) which leads to the decreased inter-fiber pore size.

Compared to the filtration efficiency, it is clearly visible that the pressure drop (Fig. 4(a) and (c), blue line) of PVA-PAA-SiO$_2$ NPs membranes was not affected to a similar extent by the different levels of SiO$_2$ NP doping. To determine the optimal formulation for air filtration performance, the quality factor (QF)\cite{14,20}, a widely used trade-off parameter (based on the experimental data of the filtration efficiency and pressure drop\cite{8}) could be calculated by the following formula:

$$QF = \frac{\ln(1 - \eta)}{\Delta P}$$

where $\eta$ is the filtration efficiency, $\Delta P$ is the pressure drop, and QF is the quality factor. From Fig. 4(b) and (d) we can conclude that the QF of PVA-PAA-SiO$_2$ NPs membranes fabricated from 4 wt% SiO$_2$ NPs are highest for both NaCl (0.029) and DEHS (0.03)) compared to other PVA-PAA-SiO$_2$ NPs nanofibrous membranes. The high efficiency is likely due to the small size and narrow diameter distribution of the PVA-PAA-SiO$_2$ NPs (4 wt%) membranes along with the high total surface area. Similar results were also obtained under more harsh conditions, where the PVA-PAA-SiO$_2$ NPs (4 wt%) membranes displayed a better performance compared to other PVA-PAA-SiO$_2$ NPs nanofibrous membranes, when tested for filtering out either NaCl or DEHS sized 300–500 nm at 85 L/min (Fig. 4S). Based
Fig. 3. Water soluble stability of the PVA-PAA nanofibrous membranes. (a) Photo of PVA-PAA (-OH: -COOH molar ratio = 1:1) nanofibrous membranes without thermal crosslinking. (b) The PVA-PAA nanofibrous membranes were immersed in water (90 °C) for 10 s. (c) The membranes dissolved in water immediately. (d) Photo of PVA-PAA (-OH: -COOH molar ratio = 1:1) nanofibrous membranes with thermally crosslinked. (e) The PVA-PAA nanofibrous membranes was immersed in water (90 °C) for 10 s. (f) The membranes were insoluble in water. The error bar stands for 1 cm.

Fig. 4. (a, c) Filtration efficiency and pressure drop, and (b, d) quality factor of PVA-PAA-SiO$_2$ NPs nanofibrous membranes (~2.55 g/m$^2$) investigated by using (a, b) NaCl and (c, d) DEHS particles (300–500 nm) under face velocity of 32 L/min.
Fig. 5. FE-SEM images of crosslinked PVA-PAA-SiO$_2$ NPs nanofibrous membranes formed with SiO$_2$ NPs concentration of (a) 0, (b) 2, (c) 4, (d) 6, and (e) 8 wt%. The molar ratio of PVA and PAA is 1:1. (f) Histogram representing the fiber diameter distribution of PVA-PAA-SiO$_2$ NPs (4 wt% SiO$_2$ NPs) nanofibrous membranes.

Fig. 6. (a) TGA of PVA-PAA-SiO$_2$ NPs (0, 2, 4, 6, 8 wt%) membranes. (b) Stress-strain behavior of PVA-PAA nanofibrous membrane and PVA-PAA-SiO$_2$ NPs (4 wt%) membrane.

Fig. 7. TEM micrographs of the PVA-PAA-SiO$_2$-Ag NPs (0.3 wt%) nanofibers with different magnification.
on these data, PVA-PAA-SiO$_2$ NPs (4 wt%) membranes were chosen as an ideal formulation for further studies.

Subsequently, in order to investigate the thermal stability of PVA-PAA-SiO$_2$ NPs nanofibrous membranes, these membranes were examined by a thermogravimetric analyzer (TGA) from 30 °C to 800 °C (under nitrogen atmosphere). As shown in Fig. 6(a), the initial thermal decomposition temperature of PVA-PAA and PVA-PAA-SiO$_2$ NPs nanofibrous membranes was around 200 °C and the rate of decomposition increased substantially in the region of 200–450 °C, which can be attributed to the degradation of the polymer backbone [1]. After 450 °C, the weight loss stabilized again, resulting in a slow decrease up to 800 °C. Moreover, as can be seen

![EDS (X ray energy spectrum) of the PVA-PAA-SiO$_2$ NPs (0.4 wt%)-Ag NPs (0.3 wt%) nanofibers membranes.](image)

**Fig. 8.** EDS (X ray energy spectrum) of the PVA-PAA-SiO$_2$ NPs (0.4 wt%)-Ag NPs (0.3 wt%) nanofibers membranes.

![Zone of inhibition of (a) *E. coli* and (b) *Bacillus subtilis*.](image)

**Fig. 9.** Zone of inhibition of (a) *E. coli* and (b) *Bacillus subtilis*. (M$_0$) PVA-PAA-SiO$_2$ NPs filter, (M$_1$) PVA-PAA-SiO$_2$ NPs – 0.1 wt% AgNO$_3$, (M$_2$) PVA-PAA-SiO$_2$ NPs – 0.2 wt% AgNO$_3$, (M$_3$) PVA-PAA-SiO$_2$ NPs – 0.3 wt% AgNO$_3$, (M$_4$) PVA-PAA-SiO$_2$ NPs – 0.4 wt% AgNO$_3$, (M$_5$) PVA-PAA-SiO$_2$ NPs – 0.5 wt% AgNO$_3$. (c) The quantification of inhibition-zone as a function with weight percentage of AgNO$_3$. 

![Zone of inhibition of *E. coli* and *Bacillus subtilis*.](image)
in Fig. 6(a), the thermal stability of the PVA-PAA-SiO2 NPs nanofibrous membranes correlated with the SiO2 NPs content, resulting in a weight loss of 43% of PVA-PAA-SiO2 NPs (4 wt%) nanofibrous membranes at 450 °C. Based on these data, it can be concluded that the PVA-PAA-SiO2 NPs nanofibrous membranes possess a certain thermal stability, up to temperatures of approximately 200 °C.

Generally, the mechanical properties of electrospun nanofibrous membranes are closely related to the geometric arrangement of the fibers, properties of the polyblend constituents, their interactions [43] and the bonds among fibers [1,22]. Fig. 6(b) shows the representative stress-strain curves of PVA-PAA and PVA-PAA-SiO2 NPs (4 wt%) nanofibrous membranes. The tensile stress of PVA-PAA membranes containing the SiO2 NPs concentration of 0 and 4 wt% were 5.20 and 8.74 MPa, respectively. As can be seen, the pure PVA-PAA membranes showed a low strength and large elongation behavior, which may be due to the rather broad distribution in fiber diameter of pure PVA-PAA membranes (Fig. 5S (a)) compared to the PVA-PAA-SiO2 NPs nanofibrous membranes (Fig. 6(f)). In these tests, the fine fibers will break first, and then the coarse fibers break later. In contrast, PVA-PAA-SiO2 NPs (4 wt%) nanofibrous membranes showed a high tensile stress compared to PVA-PAA membranes. This means that the PVA-PAA-SiO2 NPs (4 wt%) nanofibrous membranes can resist mechanical wear, enabling them to be incorporated in air filtration membranes for practical daily use.

3.3. Zone of inhibition test of PVA-PAA-SiO2 NPs-Ag NPs nanofibrous membranes

It has been reported that bacteria account for more than 80% of the inhalable microorganisms in particulate pollutants [44]. Those bacteria are likely to cause the transmission of various respiratory diseases [19,44], making air filtration membranes with antibacterial activity urgently desired [19]. As the occurrence of therapy-resistant bacterial and viral strains is increasing [45], scientists have looked at alternative methods for efficient antibacterial and antiviral therapy. Silver NPs take an important place in the spectrum of novel therapies that are widely effective against a plethora of both bacterial and viral strains [46]. As a well-known broad-spectrum antimicrobial agent [47], Ag NPs are currently the most widely commercialized nanomaterial, which are increasingly used in antimicrobial coatings [48] and consumer products [19]. To demonstrate the potential for the preparation of antibacterial air filtration membranes, Ag NPs were therefore incorporated into the electrospun membranes by the incorporation of different amounts of AgNO3 into the polymer mixture followed by UV reduction of Ag+ ions into Ag NPs. To investigate whether the Ag+ ions were successfully reduced, transmission electron microscopy (TEM) images were acquired. Ag NPs can be observed close to the surface of electrospun nanofibers (Fig. 7(a)) because Ag NPs would have migrated to the surface of the electrospun fibers along with the solvent, which diffused to the outer part of the nanofiber during the evaporation process [49,50]. The Ag NPs formed were found to be spherical (Fig. 7(b)) and were sized around 5 nm diameter (Fig. 7(c)). Via EDX analysis, it was furthermore shown that the NPs made were indeed Ag-based. (Fig. 8).

To evaluate the antibacterial efficacy of the PVA-PAA-SiO2-Ag NPs nanofibrous membranes, similar sized membranes were cut and put on top of bacterial colonies existing either of E. coli, a typical Gram-negative bacterium, or Bacillus subtilis, a typical Gram-positive bacterium. As shown in Fig. 9, the PVA-PAA-SiO2-Ag NPs nanofibrous membranes showed obvious antibacterial activities against both E. coli, and Bacillus subtilis, while Ag NP-free PVA-PAA-SiO2 NPs nanofibrous membranes did not. There was only a clear correlation between the extent of antibacterial activity and the Ag content of the electrospun fibers, at lower levels of AgNO3.
where antibacterial activity was negligible for membranes containing 0.1 wt% of AgNO₃ and appeared to reach a saturation effect for fibers containing 0.3 wt% of AgNO₃ or more. The size of the clear zone was then quantified using ImageJ. These tests were conducted in three independent repeats (Fig. 9(c) and Fig. 5S). For high production levels and to reduce the costs associated with the use of Ag, PVA-PAA-SiO₂-Ag NPs nanofibrous membranes with 0.3 wt% of AgNO₃ (M₂) were chosen as the optimal formulation for air filtration membranes.

3.4. Evaluation of cytotoxicity of green electrospun nanofibrous membranes

Next, the possible effects of the electrospun fibers were evaluated by exposing mouse fibroblast cells (L929 cell line, frequently used for cytotoxicity testing [51]) to the PVA-PAA-SiO₂-Ag NPs nanofibrous membranes. To assess the advantage of the green synthesis method employed in our current work, the “green synthesized” PVA-PAA-SiO₂ NPs-Ag NPs nanofibrous membranes were compared with the same amount of PAN₁-SiO₂ NPs-Ag NPs nanofibrous membranes and PAN₂-SiO₂ NPs-Ag NPs nanofibrous membranes which were produced with organic solvent (dimethylformamide, DMF). Both formulations contained 0.3 wt% of AgNO₃ followed by UV reduction and thermal crosslinking. As shown in Fig. 10, the viability of the L929 cells cultured with the PVA-PAA-SiO₂-Ag NPs nanofibrous membranes and PAN₁-SiO₂-Ag NPs nanofibrous membranes (may add extra cost to treat organic solvents) was much higher than that of the cells cultured with the PAN₂-SiO₂-Ag NPs nanofibrous membranes, implying no or negligible cytotoxicity of the green synthesized membranes in contrast to the higher levels of toxicity of membranes generated using hazardous organic solvents. Moreover, the result of the cytotoxicity assessment is shown in Fig. 11. Clearly, the extracts obtained from the PVA-PAA-SiO₂-Ag NPs nanofibrous membranes did not significantly influence the cell growth than PAN₁-SiO₂-Ag NPs nanofibrous membranes and PAN₂-SiO₂-Ag NPs nanofibrous membranes.

3.5. Filtration performances of PVA-PAA-SiO₂ NPs-Ag NPs nanofibrous membranes

Next, the filtration performance of PVA-PAA-SiO₂-Ag NPs (0.3 wt% AgNO₃) nanofibrous membranes was studied in depth. For this, the filtration efficiency and pressure drop of PVA-PAA-SiO₂-Ag NPs nanofibrous membranes with various base weights under a face velocity of 32 L/min were determined. The filtration efficiency of PVA-PAA-SiO₂ NPs-Ag NPs nanofibrous membranes versus increased base weight of composite membranes (1.16, 2.29, 3.16, 3.36 and 4.26 g/m²) were 49.43%, 85.63%, 93.78%, 95.34% and 98.85% for 300–500 nm non-oil NaCl particles, and 51.01%, 83.81%, 94.63%, 96.47% and 97.98% for 300–500 nm oil DEHS particles, respectively. Fig. 12(a) and (b) shows that both

![Fig. 11](image1.png)

![Fig. 12](image2.png)
the filtration efficiency and pressure drop increased with higher levels of the base weight of the PVA-PAA-SiO2-Ag NPs nanofibrous membranes. The higher base weight, achieved by extending the duration of the electrospinning process, results in a more dense network, hereby providing more contact points between particles and fibers and increased tortuous airflow channels [18,41,52]. The QF of PVA-PAA-SiO2-Ag NPs nanofibrous membranes (4.26 g/m²) was very similar for NaCl (0.0339) and DEHS (0.0384) indicating that the filtration efficiency of PVA-PAA-SiO2-Ag NPs nanofibrous membranes (4.26 g/m²) can be very high both for both non-oil particles and oil particles. As shown in Fig. 6S, the filtration efficiency of PVA-PAA-SiO2-Ag NPs nanofibrous membranes for both non-oil particles and oil particles from 300 nm to 1000 nm (PM10) was above 98%, while the filtration efficiency of PVA-PAA-SiO2-Ag NPs nanofibrous membranes for micron-sized aerosol particles can run up to 100%. As most bacteria are also in the latter size range, the high air filtration efficacy combined with potent antibacterial efficacy suggests a highly efficient antibacterial protection. This high air filtration efficiency is due to the small fiber diameter, remarkable specific surface area, interconnected porous structure and hierarchical structure of the PVA-PAA-SiO2-Ag NPs nanofibrous membranes.

Next, the filtration efficiency and pressure drop of PVA-PAA-SiO2-Ag NPs nanofibrous membranes (4.26 g/m²) as a function of face velocity were studied. Fig. 12(c) and (d) (red line), indicate that the filtration efficiency of PVA-PAA-SiO2-Ag NPs nanofibrous membranes remained stable, at more than 99% for NaCl particles and more than 98% for DEHS particles. However, the pressure drop of PVA-PAA-SiO2-Ag NPs nanofibrous membranes correlated with increasing the air flow (Fig. 12(c) and (d), blue line). The slope of the pressure drop in function of the air flow can be used to evaluate the air permeability of the filtration membranes [22]. Previous studies have reported that Darcy’s law for viscous resistance is also applicable suitable for fibrous filter medium [11], supporting our finding that the pressure drop is directly proportional to the face velocity [1,53]. Furthermore, the PVA-PAA-SiO2-Ag NPs nanofibrous membranes were tested for longitudinal exposure, undergoing a total of with 150 cycle (Fig. 13), during which the filtration efficiency was kept stable for different NaCl particle sizes. And Fig. 14(a) and (b) show one of the PVA-PAA-SiO2-Ag NPs nanofibrous membranes before and after smoke filtration. The filtration performance of the PVA-PAA-SiO2-Ag NPs nanofibrous membranes was tested using cigarette as smoke source. The PVA-PAA-SiO2-Ag NPs nanofibrous membranes turned brown when subjected to the smoke, and the effectiveness of the filtration was obvious to the naked eye.

4. Conclusion

In conclusion, we have for the first time fabricated eco-friendly crosslinked PVA-PAA composite nanofibrous membranes for combined effective air filtration and high antibacterial activity via green electrospinning. Compared to the most previously reported preparative approaches of the air filtration membranes [17,22,41], this green synthesis approach generated fibers without toxic organic solvent and did not possess any harmful cytotoxic effects and the membranes with stable high filtration efficiency (even test after 150 times). The membranes consist of hierarchically structured PVA-PAA-SiO2 NPs nanofibers to further improve the filtration performance of PVA-PAA nanofibrous membranes due to the rough surface and have a high tensile strength of more than 8.5 MPa. Further incorporation of the Ag NPs bestowed the pristine PVA-PAA-SiO2 NPs nanofibrous membranes with potent antibacterial activities against both Gram-negative (E. coli) and Gram-positive bacteria (Bacillus subtilis). The as-prepared PVA-PAA-SiO2-Ag NPs nanofibrous membranes exhibited high filtration efficiency for both non-oil aerosol and oil aerosol irrespective of the air aerosol flow. It distinguish from those of electrospun nano-fiber membranes which are only focus on filtering single aerosol (non-oil aerosol [20] or oil aerosol [42]). In addition, we assume...
that the antibacterial hierarchical air filtration membranes prepared by this green method has no toxic effect on human body. In fact, this conception is proposed and appears to be consistent with the observed data (cytotoxicity). This newly designed PVA-PAA-SiO$_2$-Ag NPs nanofibrous membranes with many superior features (e.g. high filtration efficiency, low airflow resistance, biological compatibility, and antibacterial properties) may become promising materials in the fight against polluted air, in particular for use in personal air filtration systems. What's more, we should focus on the use of some natural products or bio-based polymers for the fabrication of environmentally friendly, low-cost and non-toxic air filtration membranes with high filtration efficiency in the future work.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version, at https://doi.org/10.1016/j.jcis.2017.09.101.

References