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Antibacterial and Effective Air Filtration Membranes by "Green" Electrospinning and Citric Acid Crosslinking



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Recently, air pollution has become one of the most serious environmental problem [1,2] and is a significant health hazard to mankind [3], especially because of the haze problem caused by particulate matter (PM) which is a worldwide problem [4]. With the growing threat of air pollution, searching a cost-effective and green method to clean air is one of the most urgent challenges [5]. For personal, we just protect ourselves from PM pollutants via air filtration. Air filtration is the most promising [6] and effective approach to purify air at low costs [7]. And this abominably environmental particular matter pollution issues [8] contributed to the urgent demand for high performance air filtration media [9].

Air filters are the most common used device to remove suspended particulate matter in the air [10]. Technically speaking, conventional filtration media (micrometer-scale fibers, e.g. spun-bonded fibers, glass fibers and melt-blown fibers) [9] are incapable of capturing aerosol fine particles [11] because the pores size formed with micro-sized fibers are fairly large, and their performance are still far from satisfactory for bacterial filtration [12]. On the contrary, the nanofibrous membranes fabricated by electrospinning are displayed an excellent filtration performance (high filtration efficiency, low pressure drop) compared with traditional air filtration membranes because of their small fiber diameter, high porosity, remarkable surface area to volume ratio, interconnected pore structure [12-14]. Theoretically, nanofibers with diameters less than 500 nm [4] would boost the filtration efficiency [1] by enhanced "slip effect" [9], which is beneficial for simultaneous low airflow resistance [4]. Benefiting from those feature of electrospun nanofibrous membranes, large numbers of electrospun nanofibrous membranes have been applied in air filtration [3]. In the past few years, a wide variety of polymer such as polyamide-66 (PA-66) [15], polyacrylonitrile (PAN) [2], polyimide (PI) [16,17], polyurethane (PU) [11], polysulfone [18], polyamide-56 [19], have been successfully fabricated air filtration nanofibrous membranes [19]. Even so, it is still a big challenge to prepare air filtration membranes with high

performance, multifunctionality [4], and human friendly.

In existing electrospinning air filtration medium, not much work has been focus on human friendly and environmental friendly membranes or "green" fabrication process. Most of the polymer be used to fabricated air filtration membranes is dissolved in harmful organic solvents, which means the preparation process involves the use of harmful to highly hazardous solvents [20]. Those residual organic solvents which might be flammable [21], toxic, not environmentally friendly [22], not human friendly. During research in the laboratory, industry manufacturing, this issue causes environmental and human hazards, as well as a product for the end user [20]. This promotes the generation of "green electrospinning" technology [20,23], which could be defined as an approach which would alleviate concerns regarding safety, environmental problems and toxicology [24], could be achieved by electrospinning from aqueous polymer solution [20]. However, there is an important drawback that is the green electrospun nanofibrous membranes cannot keep stable [20] and is vulnerable to be damaged when it exposed to moist air, which should solve this problem through crosslinking technology (such as physical crosslinking, chemical crosslinking). But, many cross linkers are toxic [25] so that we should prepare the completely green membranes via physical crosslinking to avoid toxic chemical crosslinking agent (e.g. glutaraldehyde).

Herein, we explore the application of polyvinyl alcohol (PVA)/citric acid (CA) electrospun nanofibrous membranes which were prepared by green electrospinning. The aim of this work is to develop a green approach for fabricating insoluble and versatile aqueous solution based electrospun air filtration nanofibrous membranes. Simultaneously, we also incorporated hydrophobic silica nanoparticles (SiO₂ NPs) into the PVA-CA nanofibrous membranes, which could create the hierarchical roughness on the nanofiber surfaces and robust the filtration efficiency. Furthermore, we presented the fabrication of antibacterial [26,27] air filtration membranes by dropping Ag nanoparticles (Ag NPs) into the PVA-CA- SiO₂ NPs air filtration media. PVA-CA-SiO₂ NPs-Ag NPs

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Scheme 1. Schematic diagram illustrating the fabrication of PVA-CA-SiO₂ Nps-Ag NPs nanofibrous membranes by combination of electrospinning, UV reduction and thermal crosslinking. And the PVA-CA-SiO₂ Nps-Ag NPs nanofibrous membranes application for air filtration.



Fig. 1. FE-SEM images of thermally crosslinked PVA-CA nanofibrous membranes after immersed in ultra-pure water for 24 h (a) 0.2 wt% CA (PVA-CA-a), (b) 0.4 wt% CA (PVA-CA-b), (c) 0.6 wt% CA (PVA-CA-c), (d) 0.8 wt% CA (PVA-CA-d), (e) 1 wt% CA (PVA-CA-e), (f) FE-SEM images of thermally crosslinked PVA-CA (0.6 wt% CA) nanofibrous membranes.

electrospun nanofibrous membranes (Scheme 1) have been proven to be an efficient, eco-friendly, green, feasible and promising materials to the application for air filtration.

Poly(vinyl alcohol) (PVA) is a common polymer that application for air filtration membranes [28], which benefit from its physical properties [29], thermal stability [30], excellent chemical resistance [29], nontoxic [30] and complete biodegradability [29]. But a major drawback is that PVA will be dissolved immediately upon contact to water [31] after fabrication for membranes. Fortunately, PVA is a highly functional polymer (polyhydroxy polymer [29]), which gives an opportunity to modify [31]. To make the PVA membranes were rendered water-insoluble, one promising way is crosslinking of PVA via heatinduced esterification with citric acid (CA) [31,32]. And the citric acid is non-toxic and inexpensive chemicals that have used to crosslink hydroxyl bearing monomers [25]. Additionally, CA can use for air filtration membranes as well [33].

To investigate the hydrolysis stability of the PVA-CA electrospun nanofibrous membranes, the electrospun PVA-CA blend nanofibrous

membranes (with crosslinking treatment) with different mass rations were immersed in ultra-pure water for 24 h and drying before SEM. At some extent, with the increase of citric acid, the hydrolysis-resistant performance of PVA-CA nanofibrous membranes displays enhanced gradually. Fig. 1(a-e) shows the images of PVA-CA nanofibrous membranes with crosslinking treatment (different content of citric acid (0.2, 0.4, 0.6, 0.8, 1 wt%)) which were immersed in ultra-pure water for 24 h. As we can see, the PVA-CA nanofibrous membranes with crosslinking treatment (the content of citric acid is 0.6, 0.8 and 1 wt%, respectively) can maintain the original morphology preferably after immersed in water for 24 h (Fig. 1(c-e)). But compared with the PVA-CA nanofibrous membranes contained 0.2 and 0.4 wt% citric acid (PVA-CA-a and PVA-CA-b), these PVA-CA nanofibrous membranes with crosslinking treatment cannot keep stable (Fig. 1(a, b)) after immersed in water after 24 h, which was disintegrated at some extent. And the PVA membranes without citric acid (0 wt%) was immediately dissolved. Thus, we choose PVA-CA nanofibrous membranes which content 0.6 wt% citric acid (PVA-CA-c nanofibrous membranes) as the



Fig. 2. FT-IR spectrum of thermally crosslinked PVA-CA nanofibrous membranes (red line) and PVA-CA nanofibrous membranes without crosslinked (blue line). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

further research object.

The thermally crosslinking between PVA and CA occurred through esterification between hydroxyl in PVA and carboxyl in CA during heat treatment [34]. Fig. 2 show the FT-IR spectrum of thermally crosslinked PVA-CA-c nanofibrous membranes (red line) and PVA-CA-c nanofibrous membranes without crosslinked (blue line). It can be seen from the blue line that the large bands around 3320 cm⁻¹ are correspond to the –OH groups stretching from the intramolecular and intermolecular hydrogen bonds presented in Polyvinyl alcohol. The bands at 2940 cm⁻¹ and 852 cm⁻¹ are the backbone of CH₂ symmetric stretching vibration and out-of-plane twisting. And the small bands at 1097 cm⁻¹ linked to –O–H in-plane bending vibration. It also can clearly be seen from the red line that the stretching vibration of "–C=–O" (1700 cm⁻¹) becomes

stronger after thermally crosslinking, which means that the "-C=0" stretching vibration (1720 cm⁻¹) is normally shifted to the right through esterification between hydroxyl in PVA and carboxyl in CA. And the -OH groups absorption peak (at 3400 cm⁻¹) becomes weak. This proves that between polyvinyl alcohol and citric acid had a successful esterification crosslinking reaction.

To boost the air filtration performance of the PVA-CA nanofibrous membranes, we introduced the hydrophobic silica nanoparticles (SiO₂ NPs) in the PVA-CA blend solution, which created the multilevel structured of the PVA-CA electrospun nanofibrous membranes. The SiO₂ NPs can create the electrospun nanofibers membranes with the remarkably large effective surface area, high surface roughness [13]. So, the introduction of moderate SiO₂ NPs can enhance the filtration performance of nanofibrous membranes with hierarchical structures [35]. To comprehend the role of SiO₂ NPs (which create the protrusion structure [13]) in improving the air filtration performance of electrospun nanofibrous membranes, the air filtration performance (the test device as see in Fig. 1S) of the PVA-CA-SiO₂ NPs nanofibrous membranes (with the basis weight of around 2.16 g/m^2) containing various concentrations of SiO₂ NPs were systematically investigated by using the charge neutralized NaCl (sodium chloride) aerosol particles [35] and DEHS (diisooctyl sebacate) oil aerosol particles [36] in the size range of 300-500 nm under a standard airflow speed of 32 L/min, respectively. As we can see in Fig. 3(a), the filtration efficiency and pressure drop of PVA-CA-SiO2 NPs membranes obtained with the content of SiO₂ NPs of 0, 2, 4, 6 and 8 wt%, interestingly, the filtration properties of hierarchically PVA-CA-SiO₂ NPs nanofibrous membranes are distinguished from the pure PVA-CA nanofibrous membranes. The curve both in Fig. 3(a) (NaCl) and Fig. 3(c) (DEHS) presented that the filtration efficiency (the magenta line) of PVA-CA-SiO₂ NPs membranes are higher than that of PVA-CA nanofibrous membranes, achieving the maximum value of 90.407% (NaCl) and 93.095% (DEHS) at 4 wt% SiO₂ NPs, and the standard deviation along with the maximum value is 0.106 and 0.050 for NaCl and DEHS, respectively. This could be attributed to the decreasing size of average fiber diameter (Fig. 4(c) and its diameter



Fig. 3. (a) Filtration efficiency and pressure drop, and (b) quality factor of PVA-CA-SiO₂ NPs nanofibrous membranes ($\sim 2.16 \text{ g/m}^2$) investigated by using NaCl particles (300–500 nm) under face velocity of 32 L/min. (c) Filtration efficiency and pressure drop, and (d) quality factor of PVA-CA-SiO₂ NPs nanofibrous membranes ($\sim 2.16 \text{ g/m}^2$) investigated by using DEHS particles (300–500 nm) under face velocity of 32 L/min.



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Fig. 4. FE-SEM images of PVA-CA-SiO₂ NPs nanofibrous membranes (0.6 wt% CA) formed with SiO₂ NPs concentration of (a) 0, (b) 2, (c) 4, (d) 6, and (e) 8 wt%. Histogram represent the fiber diameter distribution of PVA-PAA-SiO₂ NPs nanofibrous membranes containing various concentrations of SiO₂ NPs. The electrospun nanofibers were investigated by scanning electron microscopy and image J software.



Fig. 5. TGA on PVA-CA-SiO₂ NPs (0, 2, 4, 6, 8 wt%) membranes.

distribution histogram) which are leading to the decreased pore size of the filtration membranes with 4 wt% SiO₂ NPs. Fig. 4(a–e) displayed the representative SEM images of PVA-CA-SiO₂ NPs membranes which contains different levels of SiO₂ NPs, the hierarchically structured can be found with increase the content of SiO₂ NPs. Compare to the PVA-CA-SiO₂ NPs (4 wt%) membranes, the diameter size and diameter distribution of other PVA-CA-SiO₂ NPs were found bigger and wider, which led to low filtration efficiency at the same basis weight. In contrast, compare to the filtration efficiency, it is clearly visible that the pressure drop (Fig. 3(a) and (c), blue line) of PVA-CA-SiO₂ NPs membranes are not increased sharply. The trade-off parameter of quality factor (QF) [9,15] is widely used to comprehensively evaluate the filtration performance (based on the experimental data of the filtration efficiency and pressure drop [37]) of air filtration media, and it could be calculated by the following formula:

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

where η is the filtration efficiency, ΔP is the pressure drop, and QF is the quality factor. From Fig. 4(b) and (d) we can know that, the QF of PVA-CA-SiO₂ NPs membranes fabricated from 4 wt% SiO₂ NPs are the highest (both NaCl (0.047) and DEHS (0.049)) compared to other PVA-CA-SiO2 NPs nanofibrous membranes which may due to the small size and narrow diameter distribution of the PVA-CA-SiO₂ NPs (4 wt%) membranes. What is worth mentioning, the PVA-CA-SiO₂ NPs (4 wt%) membranes displayed better performance compared to other PVA-CA-SiO₂ NPs nanofibrous membranes, which were tested at either NaCl or DEHS sized in 300–500 nm at 85 L/min (Fig. 2S). So, we would like to choose PVA-CA-SiO₂ NPs (4 wt%) membranes to do the next research.

Subsequently, in order to investigate the thermal stability of the PVA-CA, PVA-CA-SiO₂ 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. 5, the initial thermal decomposition temperature of PVA-CA and PVA-CA-SiO₂ NPs nanofibrous membranes were around 280 °C and decreased substantially in the region of 280 °C-460 °C, which can be attributed to the degradation of the polymer backbone chain [1]. It was noted that the weight of PVA-CA and PVA-CA-SiO₂ NPs nanofibrous membranes remains generally stable after 460 °C. Moreover, as can be seen in Fig. 5, the thermal stability of the PVA-CA-SiO₂ NPs nanofibrous membranes increased with the increase of SiO₂ NPs content, and the weight loss of 64% of PVA-CA-SiO₂ NPs (4 wt%) nanofibrous membranes at 460 °C. Based on the above discussion, it could be concluded that the PVA-CA-SiO₂ NPs nanofibrous membranes possess a certain thermal stability, which can resistant at least 280 °C. Generally, the mechanical properties of electrospun nanofibrous membranes were closely related to the geometric arrangement of the fibers, properties of the polyblend constituents, their interactions [38] and the bounding among fibers [1,19].

It has been reported that bacteria account for more than 80% of the inhalable particulate pollutant [39]. Those bacteria are responsible for transmission in the respiratory tract [4,39], so making air filtration membranes with antibacterial activity are urgently desired [4]. To demonstrate the potential for the preparation of antibacterial air filtration membranes, we integrated silver nanoparticles (Ag NPs). As a well-known broad-spectrum antimicrobial agent [40–42], Ag NPs are currently the most widely commercialized nanomaterial, which are increasingly used in antimicrobial coatings [43] and consumer products [4].

In the present work, the PVA-CA-SiO2 NPs-Ag NPs nanofibrous membranes obtained with the content of AgNO3 of 0.1 wt% (M1), 0.2 wt% (M₂), 0.3 wt% (M₃), 0.4 wt% (M₄), and 0.5 wt% (M₅) exhibited positive results with PVA-CA-SiO₂ NPs nanofibrous membranes, which do not show any inhibition halo. The PVA-CA-SiO₂ NPs-Ag NPs nanofibrous membranes displayed obvious antibacterial activities against E. coli. and S. aureus. As shown in Fig. 6, with the increase of Ag NPs amount, the area of inhibition zone expanded. Meaningfully, the antibacterial activity of membranes containing Ag NPs was amplified when the content of Ag NPs increased [40]. However, on account of cost and antibacterial effect, PVA-CA-SiO₂ NPs-Ag NPs nanofibrous membranes with the content of AgNO3 of 0.3 wt% (M3) has achieved good antibacterial requirements. So, we tend to use PVA-CA-SiO₂ NPs-Ag NPs (0.3 wt%) nanofibrous membranes as an air filtration membranes. And to investigate successfully reduced the Ag⁺ ions, via EDX analysis, it was furthermore shown that the NPs made were indeed Ag-based. (Fig. 7).

To thoroughly investigate the air filtration performance of PVA-CA-SiO₂ NPs-Ag NPs nanofibrous membranes, the filtration efficiency and

 $\begin{array}{l} \mbox{Fig. 6. Zone of inhibition of (a) E coli and (b) S. aureus.} \\ (M_0) $PVA-CA-SiO_2 NPs filter, (M_1) $PVA-CA-SiO_2 NPs $-0.1 wt% $AgNO_3, (M_2) $PVA-CA-SiO_2 NPs $-0.2 wt%$ $AgNO_3, (M_3) $PVA-CA-SiO_2 NPs $-0.3 wt% $AgNO_3, (M_4) $PVA-CA-SiO_2 NPs $-0.3 wt% $AgNO_3, (M_5) $PVA-CA-SiO_2 NPs $-0.5 wt% $AgNO_3.$ \end{array}$





Fig. 7. EDS (X ray energy spectrum) of the PVA-CA-SiO $_2$ NPs (0.4 wt%)-Ag NPs (0.3 wt%) nanofibers membranes.

airflow resistance (pressure drop) of PVA-CA-SiO₂ NPs-Ag NPs nanofibrous membranes with different basis weights under a face velocity of 32 L/min were tested. Fig. 8(a) and (b) show the filtration efficiency and pressure drop of the PVA-CA-SiO₂ NPs-Ag NPs nanofibrous membranes of two kinds of aerosol: non-oil particles (NaCl fine particles, 300–500 nm) and oil particles (DEHS fine particles, 300–500 nm) [11]. The filtration efficiency of PVA-CA-SiO₂ NPs-Ag NPs nanofibrous membranes versus increased basis weight of composite membranes $(1.03, 1.26, 2.00, 3.06, 4.82 \text{ and } 6.20 \text{ g/m}^2)$ were 34.416%, 52.217%, 77.778%, 94.559%, 99.832% and 99.893% for 300-500 nm NaCl particles, and 18.588%, 49.347%, 78.389%, 94.056%, 99.645% and 99.906% for 300-500 DEHS particles, respectively. It is clearly visible (Fig. 8(a) and (b)) that both the air filtration efficiency and pressure drop are increased with increasing the basis weight of PVA-CA-SiO₂ NPs-Ag NPs nanofibrous membranes, which is attributed to the prolongation of electrospinning time [35]. While the function of basis weight is more likely to help filter media to increased tortuous airflow channels and provide more contact points [13,35,44]. And the quality factor of PVA-CA-SiO₂ NPs-Ag NPs nanofibrous membranes (4.82 g/m²) was 0.0561 (NaCl) and 0.0498 (DEHS), which is very close to some extent. It means that the filtration efficiency of PVA-CA-SiO₂ NPs-Ag NPs nanofibrous membranes (4.82 g/m^2) can be very high both in nonoil particles and oil particles, and the filtration performance could keep relatively stable. What's more, as shown in Fig. 3S, the filtration efficiency of PVA-CA-SiO₂ NPs-Ag NPs nanofibrous membranes for aerosol

fine particles (both non-oil particles and oil particles) from 300 nm-1000 nm (PM $_{10}$) was above 99%, even more amazing is that the filtration efficiency of PVA-CA-SiO₂ NPs-Ag NPs nanofibrous membranes for micron level aerosol particles can run up to 100% which due to the remarkable specific surface area, small fiber diameter, interconnected porous structure and the hierarchically structure of the PVA-CA-SiO₂ NPs-Ag NPs nanofibrous membranes.

Besides, the air filtration efficiency performance of PVA-CA-SiO₂ NPs-Ag NPs nanofibrous membranes (4.82 g/m^2) under different face velocity were discussed, respectively. The results as can be seen in Fig. 8(c) and (d) (red line), the filtration efficiency of PVA-CA-SiO₂ NPs-Ag NPs nanofibrous membranes could remain stable, which could be stabilized at more than 99.8% both in NaCl particles and DEHS particles. However, the pressure drop of PVA-CA-SiO₂ NPs-Ag NPs nanofibrous membranes was increased with increasing the air flow (Fig. 8(c) and (d), blue line), whose slope could be used to evaluate the air permeability of the filtration membranes [19]. And the previous studies have reported that Darcy's law for viscous resistance is suitable for fibrous filter medium [11]. Thus the pressure drop can be directly proportional to face velocity [11]. The electrospun nanofibrous membranes possess such an excellent filtration performance due to their reticular support structure and tortuous pore channels, which allow the effective passage of air molecules, while trapping the particulate matter [45]. And when the particles in the range of $0.1-1 \,\mu m$, interception effect is the staple capture mechanism, and the collection by interception increases with increasing particle size. We should note that when the particles larger than 1 µm, inertial deposition becomes the dominant capture mechanism, especially for larger particles and at higher gas flow velocities [12].

Cytotoxicity evaluation was conducted using mouse fibroblast cell (L929) [46] through cell culture. The L929 cell is generally used for cytotoxicity assessment, which is a convenient, sensitive and standardized biomaterial [47] evaluation method to make sure whether the material releases harmful substances that significantly affect the normal cell function or whether it is cytotoxic [46]. So, we used the mouse fibroblast L929 cells to evaluate the cytotoxicity of the PVA-CA-SiO₂ NPs-Ag NPs nanofibrous membranes via green electrospinning which compared to the membranes fabricated with organic solvent (di-methylformamide, DMF) (e.g. PAN₁ (polyacrylonitrile)-SiO₂ NPs-Ag



Fig. 8. (a) Filtration performance of PVA-CA-SiO₂ NPs-Ag NPs nanofibrous membranes with different basis weight investigated by using NaCl particles (300-500 nm) under face velocity of 32 L/min. (b) Filtration performance of PVA-CA-SiO₂ NPs -Ag NPs nanofibrous membranes with different basis weight investigated by using DEHS particles (300-500 nm) under face velocity of 32 L/min. (c) Filtration performance versus face velocity of the PVA-CA-SiO₂ NPs -Ag NPs nanofibrous membranes with the basis weight of 4.82 g/m², and investigated by using NaCl particles (300-500 nm). (d) Filtration performance versus face velocity of the PVA-CA-SiO2 NPs -Ag NPs nanofibrous membranes with the basis weight of 4.82 g/m², and investigated by using DEHS particles (300-500 nm). (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.)



Fig. 9. Cytotoxicity assessment of electrospinning nanofibers membranes. Red: PVA-CA- $SiO_2\mbox{-}Ag$ NPs nanofibers membranes. Blue: $PAN_1\mbox{-}SiO_2\mbox{-}Ag$ NPs nanofibers membranes. Black: PAN2-SiO2-Ag NPs nanofibers membranes. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

NPs nanofibrous membranes which were produced with organic solvent, PAN₂-SiO₂ NPs-Ag NPs nanofibrous membranes). The residual organic solvents (DMF) of PAN1-SiO2 NPs-Ag NPs nanofibers were removed by heating the membranes for one hour (60 °C) in the vacuum. The result of the cytotoxicity evaluation is shown in Fig. 9. Clearly, the extracts obtained from the PVA-CA-SiO₂-Ag NPs nanofibrous membranes didn't significantly influence the cell growth than PAN₁-SiO₂-Ag NPs nanofibrous membranes and PAN2-SiO2-Ag NPs nanofibrous membranes, implying no or negligible cytotoxicity of PVA-CA-SiO₂-Ag NPs nanofibrous membranes. Because of the stable growth rate of L929 cells, we can conclude that the PVA-CA-SiO₂ NPs-Ag NPs nanofibrous membranes did not release harmful substances, and it is non-cytotoxic.

In summary, we have for the first time prepareed eco-friendly crosslinking PVA-PAA composite membrane for effective and antibacterial air filtration via green electrospinning. The membranes consist of hierarchical structured PVA-CA-SiO₂ NPs nanofibers to further improve the filtration performance of PVA-CA nanofibrous membranes due to the rough surface and non-circular cross section electrospun nanofibers. Further incorporation of the Ag NPs functional nanoparticles made the pristine PVA-CA-SiO₂ NPs nanofibrous membranes with antibacterial activities against both to S.aureus (Gram-positive bacterium) and E.coli. (Gram-negative bacterium). And the as-prepared PVA-CA-SiO₂ NPs-Ag NPs nanofibrous membranes exhibited high filtration efficiency (99.832%, NaCl; 99.645%, DEHS, 300-500 nm aerosol nanoparticles) and relatively low pressure drop (113.8 MPa, NaCl; 113.2 MPa, DEHS). Importantly, the PVA-CA-SiO₂ NPs-Ag NPs nanofibrous membranes are seemed very human friendly, which were no toxicity through the cytotoxicity research. This newly designed PVA-CA-SiO₂ NPs-Ag NPs nanofibrous membranes with many superior features (e.g. high filtration efficiency, low pressure droup, antibacterial and biological compatibility) may become promising materials for against the polluted air, especially application in personal protection.

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Appendix A. Supplementary Data

Supplementary data to this article can be found online at https:// doi.org/10.1016/j.colcom.2018.01.002.

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