Synthesis of Electrospun PAN/TiO$_2$/Ag Nanofibers Membrane As Potential Air Filtration Media with Photocatalytic Activity

Sri Hartati, Akmal Zulfi, Pramitha Yuniar Diah Maulida, Azis Yudhowijoyo, Mudzakkir Dioktyanto, Kurniawan Eko Saputro, Alfian Noviyanto, and Nurul Taufiqu Rochman

ABSTRACT: The PAN/TiO$_2$/Ag nanofibers membrane for air filtration media was successfully synthesized with electrospinning method. The morphology, size, and element percentage of the nanofiber were characterized by a scanning electron microscopy—energy dispersive spectroscopy, while X-ray fluorescence and FTIR were used to observe the chemical composition. The water contact angle and UV–vis absorption were measured for physical properties. Performance for air filtration media was measured by pressure drop, efficiency, and quality factor test. TiO$_2$ and Ag have been successfully deposited in nonuniform 570 nm PAN/TiO$_2$/Ag nanofibers. The nanofiber membrane had hydrophilic surface after TiO$_2$ and Ag addition with a water contact angle of 34.5°. UV–vis data showed the shifting of absorbance and band gap energy of nanofibers membrane to visible light from 3.8 to 1.8 eV. The 60 min spun PAN/TiO$_2$/Ag nanofibers membrane had a 96.9% efficiency of PM$_{2.5}$, comparable to results reported in previous studies. These properties were suitable to be applied on air filtration media with photocatalytic activity for self-cleaning performance.

INTRODUCTION

Air pollution, which consists of hydrocarbon, nitrogen oxide, and particulate matter 2.5 (PM$_{2.5}$) is harmful to the respiratory system and may even increase premature deaths.$^1$ Several studies report that high PM$_{2.5}$ concentration could cause various respiratory infections and cognitive impairment such as Alzheimer’s disease and dementia.$^2,3$ In addition, many bacteria, such as Micrococcus, Staphylococcus, and Aerococcus, are found in urban areas and also harm human health.$^4$ Wearing masks is one of the common solutions to minimize personal exposure to pollution and to prevent infection. Nowadays, the N95 facemask is one of the most effective masks used in the commercial sector with 95% efficiency. However, it is only recommended for 8 h of use and must be replaced with a new mask.$^5$ Unfortunately, the use of disposable masks increases the number of facemask waste that leads to environmental pollution.$^6$ Furthermore, it might lead to a financial burden for some people. Therefore, facemasks with self-cleaning ability and good air filtration performance are required.

Wang et al.$^7$ have recently reported that they have successfully developed PAN/TiO$_2$/Ag nanofiber membrane for application in wastewater purification. It has excellent photocatalytic activity in degrading dyes under visible light and good antibacterial activity against Escherichia coli and Staphylococcus aureus. The study demonstrates the possibility of developing nanofiber membrane with self-cleaning performance. In addition, the pure polyacrylonitrile (PAN) nanofiber membrane and PAN nanofibers with active substance are known as good air filtration media with high removal of PM$_{2.5}$.$^8$–$^{10}$

Nanofibers are one-dimensional structures having diameters of less than 1 μm.$^11$ Nanofibers have been used as high-performance air filtration because of their thin fiber diameter, wide surface area, good surface adhesion, low density, and high porosity.$^{12}$ Their pore structures are small and tortuous and are linked like a membrane, allowing collection of PM$_{2.5}$ particles from the air while minimizing pressure drop.$^{13}$

Electrospinning is one of the most common methods to synthesize nanofibers.$^{14}$ The principal components in the electrospinning process are a high-voltage source, a syringe pump, a nozzle, and a collector.$^{15}$ The continuous strand of a polymer solution is ejected through a nozzle by the high electrostatic force. Nanofibers morphology can be controlled by adjusting process parameters including high voltage, the
distance between nozzle and collector, flow rate, and the concentration of polymer solution.\(^{16}\)

In this paper, we will discuss the synthesis of the PAN/TiO\(_2\)/Ag nanofiber membrane as an air filtration media with self-cleaning properties. In our view, it is a novel development and has not been reported previously. The PAN/TiO\(_2\)/Ag nanofiber membrane will be produced through electrospinning method. Its performance will be compared to the PAN nanofiber membrane, other air filter membranes in previous studies, and commercial Semi-High Efficiency Particulate Air Filter (HEPA).

**RESULTS AND DISCUSSION**

**Characterization of the Nanofiber Membrane.** Figure 1 shows the morphology and the diameter of PAN and PAN/TiO\(_2\)/Ag nanofiber membranes.

**Figure 1.** SEM images of (a) PAN and (b) PAN/TiO\(_2\)/Ag nanofiber membranes. (c) EDS spectrum of the PAN/TiO\(_2\)/Ag nanofiber membrane.

TiO\(_2\)/Ag nanofiber membranes at 2000 times and 10000 times magnifications. On the basis of Figure 1a, the PAN nanofibers’ diameter shows normal distribution with the average of 358.9 nm, standard deviation of 0.59, and coefficient of variation (CV) 0.16. This PAN nanofiber membrane has uniform fibers since the CV value is below 0.3. On the basis of the histogram of Figure 1b, the addition of TiO\(_2\)/Ag results in an increase in the diameter of nanofibers to 570 nm followed by a wider size distribution with the CV of 0.37. This result corresponds to the results of Ren et al. and Ji et al., who reported increasing diameter of PAN after TiO\(_2\) addition.\(^{17,18}\)

Figure 1b also shows the agglomeration of TiO\(_2\)/Ag particles on the nanofiber membrane. The presence of TiO\(_2\) and Ag is shown on the SEM image as grain-like structures in the fiber. The agglomeration is due to high particle bonding among TiO\(_2\) and poor dispersion of Ag, similar to the findings of Wang et al.\(^{19}\) and Ren et al.\(^{17}\)

Figure 2 shows X-ray fluorescence (XRF) patterns of PAN and PAN/TiO\(_2\)/Ag, and XRF has been used to determine the presence of Ti and Ag. The blue line with multiple low peaks represents the PAN nanofiber membrane with no Ti and Ag in the fiber. Meanwhile, two high-intensity peaks have appeared after the addition of TiO\(_2\) and Ag. Those peaks correspond to L\(_\beta_1\) Ag at 3.011 keV and K\(_\alpha\) TiO\(_2\) at 4.533 keV.\(^{3,20-24}\)

Furthermore, to support the XRF data above, we have measured the elemental composition of the PAN/TiO\(_2\)/Ag nanofiber membrane with the energy dispersive spectroscopy (EDS) spectrum. Figure 1c shows the EDS spectrum of the PAN/TiO\(_2\)/Ag nanofiber membrane, which consists of Ti, Ag, and elements of PAN. The percentage of each element is given in Table 1. The C and N elements originate from PAN with the chemical formula (C\(_3\)H\(_3\)N)\(_n\).\(^{25}\) The O element is from the oxide of Ti. The Al element is from the aluminum foil used as the substrate of the sample.

**Figure 2.** XRF patterns of PAN and PAN/TiO\(_2\)/Ag nanofiber membranes.

**Table 1. Percentage of Elemental Composition in the PAN/TiO\(_2\)/Ag Nanofiber Membrane**

| element | wt % |
|---------|------|
| C       | 49.11|
| N       | 12.95|
| O       | 10.25|
| Al      | 2.18 |
| Ti      | 16.05|
| Ag      | 9.46 |

The FTIR spectra (absorbance) of PAN and PAN/TiO\(_2\)/Ag nanofiber membranes. The peaks between 500 and 1000 cm\(^{-1}\) on the PAN/TiO\(_2\)/Ag nanofiber membrane are from TiO\(_2\). The PAN nanofiber membrane shows characteristic peaks for the stretching vibration of the nitrile group (C≡N) at 2242 cm\(^{-1}\) and the weak ether peak (C—O—C) at 1078 and 1260 cm\(^{-1}\).\(^{26,27}\) The peaks at 1360, 1450, 1624, 2870, and 2930 cm\(^{-1}\) correspond to the vibration of aliphatic CH groups, which also originate from PAN molecules.\(^{27,31}\) After TiO\(_2\) and Ag are added, there are significant changes including two new peaks at 663 cm\(^{-1}\) related to the lattice vibration of TiO\(_2\) (Ti—O stretching)\(^{32}\) and at ~1300 cm\(^{-1}\) for TiO\(_2\)—Ag bonding.\(^{32,34}\) Accordingly, the broad peak at 1335 cm\(^{-1}\) is attributed to TiO\(_2\)—Ag bonding, which indicates that the Ag and TiO\(_2\) have been successfully deposited in the PAN
A new broad peak at 3427 cm\(^{-1}\) on PAN/TiO\(_2\)/Ag is attributed to the stretching vibration of the \(\text{−OH}\) due to the absorption of water molecules and CO\(_2\) from the air.\(^{33}\) The peaks from DMF\(^{35}\) (1677, 1388, 1092, and 659 cm\(^{-1}\)) do not appear on the PAN/TiO\(_2\)/Ag nanofiber membrane. On the basis of the result above, it can be concluded that the electrospun nanofibers do not contain residue solvent.

On a similar note, FTIR spectra indicates that there is bonding between Ag and TiO\(_2\), indicating that there are reactions between TiO\(_2\) and Ag. A previous study by Zhang et al.\(^{36}\) has reported that the incorporation of Ag into TiO\(_2\) results in partial reaction between the two substances. This reaction occurs when Ag is in the form of Ag\(^+\). In this study, AgNO\(_3\) is used as the Ag source, which would yield Ag\(^+\) ions and eventually react with TiO\(_2\). Furthermore, the existence of Ag\(^+\) ions would trap some electrons from TiO\(_2\), causing charge separation. The electrons would then be transferred to oxygen to form highly oxidative species, which would be beneficial to photocatalytic as well as antibacterial activity of the nanofiber.

A similar result has been demonstrated by Rupa,\(^{37}\) who analyzed the photodegradation performance of TiO\(_2\)/Ag nanoparticles. The key of this photocatalytic process is the photogenerated electron–hole pairs. To generate the electron, absorbed light must have sufficient energy that is equal to or larger than the band gap energy. The smaller the band gap energy is, the easier the photogenerated process will be. Absorbance of the PAN nanofiber in Figure 4a mostly occurs with a wavelength of less than \(\sim 300\) nm, which is in the UV light region. Meanwhile, the PAN/TiO\(_2\)/Ag nanofiber membrane is able to absorb light with a higher wavelength up to 400 nm, which is in the visible light region.

Furthermore, Figure 4b displays the band gap energy plots of the PAN and PAN/TiO\(_2\)/Ag nanofiber membranes, which show the shifting band gap energy of the PAN nanofiber membrane from 3.8 to 1.8 eV. The mechanism of band gap shifting in TiO\(_2\)/Ag has also been reported by several studies.\(^{24,32,37}\) Under visible light, Ag acts as a photosensitizer, collecting the visible light to generate the electron to the conduction band of TiO\(_2\). The charge separation generated by the existence of Ag would create sites near the conduction band of TiO\(_2\). The shifting of the Fermi energy nearer to the conduction band would result in the narrowing of the band gap energy, thus improving the photocatalytic activity. The improvement in photocatalytic activity is also supported by various studies that demonstrate TiO\(_2\)/Ag to have good photocatalytic activity under visible light.\(^{7,23,33,38−40}\)

Photocatalytic properties of PAN/TiO\(_2\)/Ag are related to the membrane’s ability in dye degradation. Irradiating each sample with UV and visible light enables further observations. Table 2 shows the results of exposing the PAN nanofiber membrane and the PAN/TiO\(_2\)/Ag nanofiber membrane samples to UV light for 1 h after adding methylene orange and methylene blue solutions. The PAN nanofiber membrane shows excellent dye degradation on 60 ppm methylene orange drops after 1 h of UV irradiation. However, the degradation with 80 ppm methylene orange drop does not reach completion. The degradation is because of PAN’s chemical properties as a polymer that can serve as a photocatalyst.\(^{41−43}\) Meanwhile, the methylene blue droplets on the PAN nanofiber membrane only slightly degrade after 1 h of irradiation. On the other hand, the PAN/TiO\(_2\)/Ag nanofiber membrane loses all of its dyes and turns brown as if it has been burned. It can be explained that the burning of nanofiber membrane is due to the existence of Ag which is oxidized and browned after UV irradiation.

Table 3 shows the color degradation of methylene blue under visible light on the PAN nanofiber membrane and the
PAN/TiO₂/Ag nano-fiber membrane after adding 60 and 80 ppm methylene blue, respectively. The 60 ppm methylene blue dyes on the PAN/TiO₂/Ag nano-fiber membrane fade and disappear within 20 min. Meanwhile, the 80 ppm methylene blue vanishes within 25 min under visible light. In addition, the color of methylene orange at the concentration of 60 ppm completely vanishes after 25 min under visible light. Meanwhile, at the 80 ppm concentration, it disappears within 30 min.

Wang et al. reported that dye degradation of the PAN/TiO₂/Ag nano-fiber membrane depends on the chemical structure and properties of the pollutants. Therefore, the difference in degradation time between methylene blue and methylene orange is affected by their properties. Thus, the PAN/TiO₂/Ag nano-fiber membrane photocatalytic is proven to occur under visible light irradiation.

The wettability of samples can be characterized by observing the water contact angle on the membrane’s surface. It represents the hydrophobicity and hydrophilicity of the surface. A hydrophobic surface can be observed when the contact angle is higher than or equal to 90°. Meanwhile, a hydrophilic surface has a contact angle lower than 90°. A hydrophobic surface has a contact angle lower than 90°. Figure 5 shows the water contact angle on the PAN and PAN/TiO₂/Ag nano-fiber membranes. As shown in Figure 5a, the surface of the PAN nano-fiber membrane yields the nearly spherical shape of a sessile drop with a 123.56° contact angle. This indicates that the PAN nano-fiber membrane can be categorized as a hydrophobic membrane. On the other hand, the PAN/TiO₂/Ag nano-fiber membrane has a 34.58° contact angle, as shown in Figure 5b, indicating that the PAN/TiO₂/Ag nano-fiber membrane is hydrophilic. It has been confirmed that the hydrophobic PAN nano-fiber membrane became hydrophilic after the addition of TiO₂/Ag. This is due to the existence of TiO₂, in accordance with several studies about TiO₂ as nanoparticles or nanotube or nano-fibers that show a water contact angle lower than 90° and consistently provide hydrophilic surface. Moreover, the addition of Ag to TiO₂ decreases the optical band gap of TiO₂, thus, photocatalytic TiO₂ and Ag are easier to react with water under visible light, which potentially forms the hydrophilic surface. Self-cleaning based on the hydrophilic surface is achieved by the photocatalytic role, which is usually generated by TiO₂. Several studies have reported that the photogenerated hole of TiO₂ reacts with water in 1 μs and the electron capture reaction enhances the water absorption. These reports indicate that the PAN/TiO₂/Ag nano-fiber membrane can react with water. Thus, the PAN/TiO₂/Ag nano-fiber membrane becomes hydrophilic.

### Table 2. Degradation of Dyes under UV Light for 60 min on a Nanofiber Membrane

| Concentration | Methylene Orange | Methylene Blue |
|---------------|------------------|----------------|
| 60 ppm        | ![Image](image1.png) | ![Image](image2.png) |
| 80 ppm        | ![Image](image3.png) | ![Image](image4.png) |

“PAN on the left side of each the pictures and PAN/TiO₂/Ag on the right side of each the pictures (photos were taken by Sri Hartati).

### Table 3. Degradation of Methylene Blue under Visible Light for Several Minutes on a Nanofiber Membrane

| Dyes         | Concentration | Times |
|--------------|---------------|-------|
| Methylene Blue | 60 ppm        | ![Image](image5.png) |
|              | 80 ppm        | ![Image](image6.png) |
| Methylene Orange | 60 ppm      | ![Image](image7.png) |
|              | 80 ppm        | ![Image](image8.png) |

“PAN on the left side of each the pictures and PAN/TiO₂/Ag on the right side of each the pictures (photos were taken by Sri Hartati).
In the air filter application, the hydrophobic membrane is excellent as an air filter because its self-cleaning surface allows the water droplets to roll up particles on the surface easily. But this process only cleanses the surface of the membrane, while the trapped particle on the fiber sidelines is not removed in this self-cleaning process. The hydrophilic nano fiber membrane can clean up the particle on the sideline with the photocatalytic process. It yields reactive oxygen species that can oxidize the organic molecules and kill the bacteria. In addition, TiO₂ and Ag have been reported to have high antibacterial activity.

**Air Filtration Performance.** Particulate air filters are classified into two categories based on the position of the captured particles including surface filters and depth filters. A surface filter is the common filtration hindering the particles larger than the pores of the membrane. The particle can be made from metal wire mesh, a perforated plate, or a chemical porous membrane (cellulose acetate). Meanwhile, on the depth filters, particle capturing is on the inside medium layer. A depth filter with a high solid fraction is formed by granular filling layers, porous filter media, and thick fiber paper. On the other hand, a depth filter with a low solid fraction generally forms a fibrous filter, a thin paper air filter with high efficiency, a foam media filter, etc. A membrane filter in nanofiber form has many advantages to filter ultrafine particles. Woven or nonwoven nano fiber membrane filtration with porosity is highly capable of filtering PM_{2.5} in the air. The performance of a nano fiber membrane as filtration media can be evaluated by several parameters, such as quality factor, efficiency, and pressure drop.

Pressure drop is one important parameter that must be considered in air filtration application. The pressure drops, or pressure gradient along the airflow direction across the nano fiber membrane, have a direct impact on the air filtration performance. An ideal air filtration system must have both high efficiency and low pressure drop. However, the high efficiency of air filtration is often accompanied by a high pressure drop. Good air filtration must have a linear plot between the pressure drop and face velocity as well as obtain a straight line on data plotting (ΔP) against face velocity which follows Darcy’s law. Figure 6 shows the linear fitting pressure drop of PAN and PAN/TiO₂/Ag nanofiber membranes. According to Figure 6, the PAN nano fiber membrane has a higher pressure drop than the PAN/TiO₂/Ag nano fiber membrane for the same spinning time. This is due to the small pores possessed by the PAN nano fiber membrane with small average size nanofibers. The small pores hinder the air flow through the membrane, which leads to an increase in the pressure drop.

Meanwhile, the PAN/TiO₂/Ag nano fiber membrane shows a lower pressure drop than the PAN nano fiber membrane. It is due to the wide diameter distribution and morphology of the nanofibers. On the basis of the SEM image (Figure 1b), the fiber diameter varies widely from 100 to 1200 nm, with an average diameter of 570 nm. The existence of large nanofibers among small PAN/TiO₂/Ag nano fiber membrane creates space between them. It provides the pathways for air to flow through the membrane. Therefore, the air particles easily pass through the membrane, which leads to the lowering of the pressure drop. On the other hand, the PAN/TiO₂/Ag nano fiber membrane (spun for 60 min) shows the highest pressure drop. It is acceptable since additional time increases the thickness of the membrane. In general, when the morphology of nanofibers is uniform, the thick membrane yields a high pressure drop since the membrane passes less air. Furthermore, increasing the membrane thickness will improve its ability to capture particles, leading to higher efficiency of the PAN/TiO₂/Ag nano fiber membrane.

Efficiency is another parameter to determine good air filtration media. The efficiency of PM_{2.5} has been measured to test the air filter performance of the PAN and PAN/TiO₂/Ag nano fiber membranes. Incense smoke used in this study as PM_{2.5}, as it represents a real pollutant. Table 4 shows that the PAN/TiO₂/Ag nano fiber membrane has a lower efficiency on filtering the PM_{2.5} than the PAN nano fiber membrane, both spun for 30 min. This is due to the PAN nano fiber membrane composition, which consists of the uniform small nanofiber. As mentioned above, the small size fiber of the PAN nano fiber...
Table 4. Filtration Efficiency of PM2.5 of PAN and PAN/TiO2/Ag Nanofiber Membranes

| test | PAN* | PAN/TiO2/Ag* | PAN/TiO2/Ag* |
|------|------|-------------|-------------|
| 1    | 81.7 | 58.8        | 94.9        |
| 2    | 82.7 | 58.7        | 96.9        |
| 3    | 82.4 | 59.5        | 97.6        |
| 4    | 82.7 | 61.7        | 97.7        |
| 5    | 83.2 | 62.9        | 97.4        |

mean 82.6 ± 1.3 60.3 ± 0.4 96.9 ± 2.7

*Spin for 30 min. *Spin for 60 min.

membrane produces small pores. Furthermore, the small pores will effectively capture the particles, indicating the enhanced efficiency of the membrane. Meanwhile, the PAN/TiO2/Ag nanofiber membrane has nonuniform diameter distribution, causing the existence of large pores. These large pores will pass more air particles, which lowers the efficiency of the membrane.56,58 Indeed, increasing the spinning process will increase the efficiency of the membrane. A 96.9% efficiency has been obtained for the PAN/TiO2/Ag membrane for 60 min of spinning, as shown in Table 4.

The filtering efficiency of NaCl particles has also been measured in this study. Figure 7 shows the efficiency of the 30 min spinning of PAN and PAN/TiO2/Ag nanofiber membranes for NaCl particles with a diameter range of 24–362 nm. For fine particle air filtration, there are three particle capturing mechanisms including diffusion, interception, and impaction. The diffusion mechanism is based on the Brownian motion caused by the collision of gas molecules and particles.54

Particles that move by Brownian diffusion in their direction can deviate from the air flow through the fiber and then hit and stick to the nanofiber.55,62

The interception mechanism occurs when the particle with a certain size is not captured by Brownian diffusion.62 The particle will follow the streamline of air flow perfectly and deposit on the fiber due to interception effect by the fiber.63 The particle will touch the fiber directly when the distance of particle is half of the diameter of the fiber.63 Meanwhile, the impaction mechanism occurs when the particle could not capture via the Brownian diffusion and interception mechanism. The particle will deviate from the streamline air flow due to the inertial effect of the particle or the impact of the external forces, electric or gravitational.61,63

Mostly, the particles below 100 nm are collected by the diffusion mechanism, while interception and impaction are effectively involved with particles sizes of 500 nm or above.59,64,65 The combination of three mechanisms will yield the efficiency graph, as shown in Figure 7. From this graph, the most penetrating particle size (MPPS) can be determined along with the particle size at the lowest efficiency. In general, the MPPS range is between 50 and 500 nm.60,69 The MPPS of both the PAN/TiO2/Ag nanofiber membrane and the PAN nanofiber membrane are 98.84 nm. However, the small pores of the PAN nanofiber membrane effectively capture the particles, resulting in a higher efficiency PAN nanofiber membrane in comparison to the PAN/TiO2/Ag nanofiber membrane.

Comparison with a Previous Study. In this study, we also compare the PAN/TiO2/Ag nanofiber membrane with previous study about filter membrane. It has explored the possibility of membrane application as respirator media. The comparison takes into account the quality factor of each membrane: the higher the quality factor, the better the membrane quality. For this, we have used the PAN/TiO2/Ag nanofiber membrane for 60 min of spinning due to the higher pressure drop and efficiency.

Figure 8 shows the comparison of the quality factor of the PAN/TiO2/Ag nanofiber membrane followed by membranes reported in other studies with PM2.5 as flow particles. The gray bar represents our sample, whereas the red bars are from the literature. Bowin95 (commercial mask), Bowin99 (commercial mask), and ABS are the air filter membranes, which have been reported by Zulfie et al.56 Meanwhile, the PVA, PVDF, PAN (nanofiber based filter), and commercial Semi-HEPA filter has been reported by Kim.65 The quality factor can be calculated with the following formula:

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

where \(\eta\) is the efficiency and \(P\) is the pressure drop of the membrane.
According to Figure 8, the PAN/TiO₂/Ag nanofiber membrane has a 2.45 × 10⁻² Pa⁻¹ quality factor. It is almost at the same level with the ABS air filter membrane. This quality factor is higher than the quality factor of a commercial mask and other air filtration media. On the basis of this result, we are optimistic that the PAN/TiO₂/Ag nanofiber membrane can be applied as air filtration media with self-cleaning ability.

**EXPERIMENTAL SECTION**

**Material and Synthesis.** PAN and N,N-dimethylformamide (DMF) were purchased from Sigma-Aldrich, Singapore. TiO₂ and AgNO₃ from Merck were purchased from a local supplier. The fabrication of nanofiber membrane was using electrospinning, which had been used by Zulfi et al.⁵⁶ The precursor solution was dissolved with DMF by a magnetic stirrer at 50 °C for 12 h with specific concentrations based on Table 5.

**Table 5. Precursor Solution for PAN and PAN/TiO₂/Ag Nanofiber Membranes**

| precursor   | PAN | TiO₂ | Ag |
|------------|-----|------|----|
|            | 10 wt % | 0.5 wt % | 2 wt % |
| PAN/TiO₂/Ag | 10 wt % | 0.5 wt % | 2 wt % |

The precursor solution was poured into a 10 mL syringe with an 0.8 mm inner diameter needle. It was placed on the electrospinning syringe pump with a 15 cm long distance to the rotary drum collector. The drum collector had a 5.5 cm diameter and a 12 cm length. It was wrapped with aluminum foil to facilitate nanofiber collection. A high voltage of 15 kV and flow rate of 0.5 mL/h were applied in this process.

**Characterization.** The morphology and size of the PAN/TiO₂/Ag nanofiber membranes were investigated using a scanning electron microscope (SEM Thermoscientific Quanta 650) with 2000 times and 10000 times magnifications. SEM images of the nanofibers were analyzed using the Image MIsoftware to obtain the size distribution of nanofibers on 100 fibers randomly. The average distribution diameter was analyzed statistically. The fiber uniformity was determined from the coefficient of variation (CV) given as follows.

\[
CV = \frac{\sigma_f}{\mu_f}
\]

where \(\sigma_f\) is the standard deviation and \(\mu_f\) is the average fiber diameter. The value of CV below 0.3 indicated that the nanofibers were uniform while above 0.3 indicated nonuniform nanofibers.⁶⁹

The presence of the Ti and Ag was observed using X-ray fluorescence (XRF Rigaku NEX OC+ EZ series number QC1520) with an operating range between 2000 and 15000 keV. The EDS spectrum (SEM Thermoscientific Quanta 650) was used to confirm the percentage of the PAN/TiO₂/Ag nanofiber membrane elemental composition.

The functional groups in the PAN/TiO₂/Ag nanofiber membrane were analyzed using Fourier transform infrared spectrometry (Thermo-fisher Scientific NICOLET IS10 FTIR spectrometer) with a spectral range of 500—4000 cm⁻¹. The absorbance of PAN and PAN/TiO₂/Ag nanofiber membranes was characterized by a double beam UV—vis spectrometer (Labtron LUS-B13 series number M18P21090201).

The wettability of PAN and PAN/TiO₂/Ag nanofiber membranes was determined by examining the surface characteristics through the measurement of the water contact angle by using a contact angle meter (CAAI 2320). The 5 μL water droplet was dropped from the needle, which was controlled by a syringe pump after the sample was placed in the holder. Then the droplet on the surface was captured by a camera. The examination was done on five repetitions.

**Air Filter Performance.** Pressure drop, the efficiency of NaCl particles, the efficiency of PM2.5 particles, and the quality factor of the fabricated nanofiber membrane were measured in this study. Pressure drop and PM2.5 efficiency were measured according to the procedure by Zulfi et al.⁵⁶ Figure 51 shows the scheme of the air filtration test system for the efficiency of NaCl particles. Before the NaCl particles with various size were flowed to the membrane, the charge of aerosols (NaCl particles) was dried and neutralized with a concentration below 10 000 particles per cm³. The measurement of the particles with and without samples was averaged for each condition. The efficiency of filtration was measured by comparing the average deviation of the particles without a membrane according to the standard particle filtration method, which was explained in ASTM F2299. It was done with 5.3 cm/s of face velocity, 1.6 LPM of Q_IN, 5 LPM of Q_DIL, and 1 LPM of Q_AE. The entire test was using 5.3 cm/s face velocity, which was commonly accepted as an air filtration test standard.

**CONCLUSIONS**

PAN/TiO₂/Ag nanofiber membrane has been successfully synthesized through the electrospinning method. The resulting samples are the PAN nanofiber membrane before and after addition TiO₂/Ag. Morphology of the PAN nanofiber membrane shows the uniform distribution, while the PAN/TiO₂/Ag nanofiber membrane is nonuniform. The EDS and XRF graphics show the peaks of Ti and Ag, which indicate that Ti and Ag are successfully deposited onto the PAN nanofibers. The FTIR spectra show Ti and Ag bonding is obtained. It also confirms that the PAN/TiO₂/Ag nanofiber membrane has a bonding with water molecules. Furthermore, addition of TiO₂ and Ag causes conversion of the hydrophobic PAN to be hydrophilic. It also shifts the absorbance and band gap energy to visible light. According to an air filtration performance test, the PAN/TiO₂/Ag nanofiber membrane after 60 min spinning has the highest efficiency of 96.9% for PM2.5. Its quality factor is better than those of commercial masks and several air filters from other research. We conclude that the PAN/TiO₂/Ag nanofiber membrane has the potential to be used as an air filtration medium with self-cleaning properties.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.2c00015.

Schematic diagram of air filtration test (Figure S1) and the complete results of Table 4 (PDF)

**AUTHOR INFORMATION**

**Corresponding Author**

Akmal Zulfi — Nano Center Indonesia, South Tangerang, Banten 15314, Indonesia; National Research and Innovation Agency, Central Jakarta City 10340, Indonesia;
Complete contact information is available at:

scopus.scopus.com/record.uri?eid=2-s2.0-85067011985&partnerID=40&md5=5a357d854ed8b595cb36c0d909f8c899

Appl. Environ. Microbiol. 2019, 85, 10523–10530.

This study was financially supported by the Indonesian Endowment Funds for Education, The Ministry of Finance, Republic of Indonesia. The authors thank the Nano Center Indonesia for the facilities and characterization. We also acknowledge the Center of Aerosol and Analytical Instrumentation (CAAI) Laboratory as the owner of electrospinning, contact angle meter and the instrument of air filtration performance test.

ACKNOWLEDGMENTS

This study was financially supported by Mandatory Productive Innovative Research Funding No. KEP-53/LPDP/2020 by Indonesian Endowment Funds for Education, The Ministry of Finance, Republic of Indonesia. The authors express their gratitude to the Nano Center Indonesia for the facilities and characterization. We also acknowledge the Center of Aerosol and Analytical Instrumentation (CAAI) Laboratory as the owner of electrospinning, contact angle meter and the instrument of air filtration performance test.

REFERENCES

(1) Mauzerall, D.; Communications, N. A Conversation on the Impacts and Mitigation of Air Pollution. Nat. Commun. 2021, 12 (1), S821.

(2) Croft, D. P.; Burton, D. S.; Nagel, D. J.; Bhattacharya, S.; Falsey, A. R.; Georas, S. N.; Hopke, P. K.; Johnston, C. J.; Kottmann, R. M.; Litonjua, A. A.; Mariani, T. J.; Rich, D. Q.; Thevenet-Morrison, K.; Thurston, S. W.; Utell, M. J.; McCall, M. N. The Effect of Air Pollution on the Transcriptomics of the Immune Response to Airborne Bacteria in an Urban Environment. Appl. Environ. Microbiol. 1978, 35 (6), 1095–1101.

(5) Alagöz, S.; Bal, K. K.; Ozdas, T.; Delibas, V.; Kuran, G.; Ekcı, N. Y.; Gorgulu, O.; Oztornac, R. O. Effect of Using N95 and Surgical Masks on Otoacoustic Emission in Cochlear Outer Hair Cells. Ear, Nose Throat J. 2021, DOI: 10.1177/01455613211034600.

(6) Aragaw, T. A. Surgical Face Masks as a Potential Source for Microplastic Pollution in the COVID-19 Scenario. Mar. Pollut. Bull. 2020, 159 (July), 111517.

(7) Wang, L.; Ali, J.; Zhang, C.; Mailhot, G.; Pan, G. Simultaneously Enhanced Photocatalytic and Antibacterial Activities of TiO2/Ag Composite Nanofibers for Wastewater Purification. J. Environ. Chem. Eng. 2020, 8 (1), 102104.

(8) Song, Y.; Wang, Y.; Xu, L.; Wang, M. Fabrication and Characterization of Electrospun Porous PAN/Graphene Composite Nanofibers. Nanomaterials 2019, 9 (12), 1782.

(9) Roche, R.; Yalcinkaya, F. Electrospun Polycaprolactone Nanofibrous Membranes for Point-of-Use Water and Air Cleaning. ChemistryOpen 2019, 8 (1), 97–103.

(10) Liu, C.; Hsu, P. C.; Lee, H. W.; Ye, M.; Zheng, G.; Liu, N.; Li, W.; Cui, Y. Transparent Air Filter for High-Efficiency PM 2.5 Capture. Nat. Commun. 2015, 6, 1–9.

(11) Zdraveva, E.; Fang, J.; Mijovic, B.; Lin, T. Electrospun Nanofibers. Structure and Properties of High-Performance Fibers; Elsevier Ltd: Amsterdam, 2017; pp 267–300, DOI: 10.1016/B978-0-08-100550-7.00011-5.

(12) Zhang, S.; Rind, N. A.; Tang, N.; Liu, H.; Yin, X.; Yu, J.; Ding, B. Electrospun Nanofibers for Air Filtration. Electrospinning: Nanofabrication and Applications; Elsevier Inc.: Amsterdam, 2018; pp 365–389, DOI: 10.1016/B978-0-323-51270-1.00012-1.

(13) Zhao, X.; Wang, S.; Yin, X.; Yu, J.; Ding, B. Slip-Effect Functional Air Filter for Efficient Purification of PM 2.5. Sci. Rep. 2016, 6, 35472.

(14) Li, D.; Xia, Y. Electrospinning of Nanofibers: Reinventing the Wheel? Adv. Mater. 2004, 16 (14), 1151–1170.

(15) Munir, M. M.; Suryamas, A. B.; Iskandar, F.; Okuyama, K. Scaling Law on Particle-to-Fiber Formation during Electrospinning. Polymer (Guildf). 2009, 50 (20), 4935–4943.

(16) Munir, M. M.; Iskandar, F.; Djamal, M.; Okuyama, K. Morphology Controlled Electrospun Nanofibers for Humidity Sensor Application. AIP Conf. Proc. 2011, 1415 (2011), 223–226.

(17) Ren, H. T.; Han, J.; Li, T. T.; Liang, Y.; Jing, M. Z.; Jiang, S. M.; Lin, J. H.; Lou, C. W.Facile Preparation of PAN@Ag−Ag2O/TiO2 Nanofibers with Enhanced Photocatalytic Activity and Reusability toward Oxidation of As(III). J. Mater. Sci. 2020, 55 (25), 11310–11324.

(18) Ji, B. C.; Bae, S. S.; Rabbani, M. M.; Yeum, J. H. Photocatalytic Activity of Electrospun PAN/TiO2 Nanofibers in Dye Photodecomposition. Text. Color. Finish. 2013, 25 (2), 94–101.

(19) Wang, S. D.; Ma, Q.; Liu, H.; Wang, K.; Ling, L. Z.; Zhang, K. Q. Robust Electrospinning Cellulose acetate@TiO2 Ultrafine Fibers for Dyeing Water Treatment by Photocatalytic Reactions. RSC Adv. 2015, 5 (51), 40521–40530.

(20) Baharvand, A.; Ali, R.; Nur, H. Imazalil Sulphate Pesticide Degradation Using Silver Loaded Hollow Anatase TiO2 under UV Light Irradiation. Malaysian J. Fundam. Appl. Sci. 2016, 12 (2), 60–67.

(21) Dakhel, a. a. Critical Role of Hydrogenation for Creation of Magnetic Co-Cu Co-Incorporated TO2 Nanocrystallites. Appl. Phys. A Mater. Sci. Process. 2020, 126 (1), 1–8.

(22) Liu, W.; Chen, D.; Yoo, S. H.; Cho, S. O. Hierarchical Visible-Light-Response Ag/AgCl@TiO2 Plasmonic Photocatalysts for Organic Dye Degradation. Nanotechnology 2013, 24 (40), 405706.

(23) Lee, M. S.; Hong, S. S.; Mohseni, M. Synthesis of Photocatalytic Nanosized TiO2-Ag Particles with Sol-Gel Method Using Reduction Agent. J. Mol. Catal. A. Chem. 2005, 242 (1–2), 135–140.

(24) Gomes, a.; Videira, a.; Monteiro, O. C.; Nunes, C. D.; Carvalho, M. L.; Lopes, a. B. Pulsed Current Electrodeposition of Zn-Ag2S/TiO2 Nanocomposite Films as Potential Photocatalysts. J. Solid State Electrochem. 2013, 17 (8), 2349–2359.
(25) Yu, D. G.; Zhou, J.; Chatterton, N. P.; Li, Y.; Huang, J.; Wang, X. Polycrylonitrile Nanofibers Coated with Silver Nanoparticles Using a Modified Coaxial Electrospinning Process. Int. J. Nanomedicine 2012, 7, 5725−5732.

(26) Zhao, J.; Zhang, J.; Zhou, T.; Liu, X.; Yuan, Q.; Zhang, A. New Understanding on the Reaction Pathways of the Polycrylonitrile Copolymer Fiber Pre-Oxidation: Online Tracking by Two-Dimensional Correlation FTIR Spectroscopy. RSC Adv. 2016, 6 (6), 4397−4409.

(27) Nguyen-Thai, N. U.; Hong, S. C. Structural Evolution of Poly(acrylonitrile-Co-Itaconic Acid) during Thermal Oxidative Stabilization for Carbon Materials. Macromolecules 2013, 46 (15), 5882−5889.

(28) Ge, Y.; Fu, Z.; Zhang, M.; Zhang, H. The Role of Structural Evolution of Polycrylonitrile Fibers during Thermal Oxidative Stabilization on Mechanical Properties. J. Appl. Polym. Sci. 2021, 138 (1), 49603.

(29) Dang, W.; Liu, J.; Wang, X.; Yan, K.; Zhang, A.; Yang, J.; Chen, L.; Liang, J. Structural Transformation of Polycrylonitrile (PAN) Fibers during Rapid Thermal Pretreatment in Nitrogen Atmosphere. Polymers (Basel) 2020, 12 (1), 63.

(30) Zhang, C.; Yao, L.; Yang, Z.; Kong, E. S. W.; Zhu, X.; Zhang, Y. Graphene Oxide-Modified Polycrylonitrile Nanofibrous Membranes for Efficient Air Filtration. ACS Appl. Nano Mater. 2019, 2 (6), 3916−3924.

(31) Chai, X.; Mi, H.; Zhu, C.; He, C.; Xu, J.; Zhou, X.; Liu, J. Low-Temperature Thermal Stabilization of Polycrylonitrile-Based Precursor Fibers towards Efficient Preparation of Carbon Fibers with Improved Mechanical Properties. Polymer (Guildf.) 2015, 76, 131−139.

(32) Alsharaeh, E. H.; Bora, T.; Soliman, a.; Ahmed, F.; Bharath, G.; Ghoniem, M. G.; Abu-Salah, K. M.; Dutta, J. Sol-Gel-Assisted Microwave-Derived Synthesis of Anatase Ag/TiO2/Go Nanohybrids toward Efficient Visible Light Photocatalytic Degradation. Catalysts 2017, 7 (5), 133.

(33) Wang, Y.; Yan, L.; He, X.; Li, J.; Wang, D. Controlled Fabrication of Ag/TiO2 Nanofibers with Enhanced Stability of Photocatalytic Activity. J. Mater. Sci. Mater. Electron. 2016, 27 (5), 5190−5196.

(34) Desiati, R. D.; Taspika, M.; Sugarti, E. Effect of Calcination Temperature on the Antibacterial Activity of TiO2/Ag Nano-composite. Mater. Res. Express 2019, 6 (9), 095059.

(35) Shastri, A.; Das, A. K.; Krishnakumar, S.; Singh, P. J.; Raja Sekhar, B. N. Spectroscopy of N, N-Dimethylformamide in the VUV and IR Regions: Experimental and Computational Studies. J. Chem. Phys. 2017, 147 (22), 224305.

(36) Zhang, X.; Ly, Y.; Cai, G.; Fu, S.; Yang, L.; Ma, Y.; Dong, Z. Reactive Incorporation of Ag into Porous TiO2 Coating and Its Influence on Its Microstructure, in Vitro Antibacterial Efficacy and Cytocompatibility. Proc. Nat. Sci. Mater. Int. 2021, 31 (2), 215−229.

(37) Rupa, A. V.; Manikandan, D.; Divakar, S.; Sivakumar, T. Effect of Deposition of Ag on TiO2 Nanoparticles on the Photodegradation of Reactive Yellow-17. J. Hazard. Mater. 2007, 147 (3), 906−913.

(38) Sanzome, G.; Zimbone, M.; Cacciato, G.; Ruffino, F.; Carles, R.; Privitera, V.; Grimaldi, M. G. Ag/TiO2 Nanocomposite for Visible Light-Driven Photocatalysis. Superlatives Microstruct. 2018, 123, 394−402.

(39) Chakhtouna, H.; Benzeid, H.; Zari, N.; Qais, A. E. K.; Bouhdid, R. Recent Progress on Ag/TiO2 Photocatalysts: Photocatalytic and Bactericidal Behaviors. Environ. Sci. Pollut. Res. 2021, 28 (33), 46438−46466.

(40) Saud, P. S.; Ghouri, Z. K.; Pant, B.; An, T.; Lee, J. H.; Park, M.; Kim, H. Y. Photocatalytic Degradation and Antibacterial Investigation of Nano Synthesized Ag3V04 Particles @PAN Nanofibers. Carbon Lett. 2016, 18 (1), 30−36.

(41) Banerjee, T.; Podjaski, F.; Kröger, J.; Biswal, B. P.; Lotsch, B. V. Polymer Photocatalysts for Solar-to-Chemical Energy Conversion. Nat. Rev. Mater. 2021, 6, 168.
(59) Hung, C. H.; Leung, W. W. P. Filtration of Nano-Aerosol Using Nanofiber Filter under Low Peclet Number and Transitional Flow Regime. Sep. Purif. Technol. 2011, 79 (1), 34−42.

(60) Zulfi, A.; Hapidin, D. A.; Saputra, C.; Mustika, W. S.; Munir, M. M.; Khairurrijal, K. The Synthesis of Fiber Membranes from High-Impact Polystyrene (HIPS) Waste Using Needleless Electrospinning as Air Filtration Media. Mater. Today Proc. 2019, 13, 154−159.

(61) Bunawas, O. P. Penentuan Efisiensi Filter Hepa Dengan Aerosol Dioctyl Pthalate. Presidin Presentasi Ilmiah Keselamatan Radiasi dan Lingkungan 1996, 8, 114−122.

(62) Podgórski, A.; Balazy, A.; Gradoń, L. Application of Nanofibers to Improve the Filtration Efficiency of the Most Penetrating Aerosol Particles in Fibrous Filters. Chem. Eng. Sci. 2006, 61 (20), 6804−6815.

(63) Chen, C. Y. Filtration of Aerosols by Fibrous Media. Chem. Rev. 1955, 55 (3), 595−623.

(64) Mostofi, R.; Noel, A.; Haghighat, F.; Bahloul, A.; Lara, J.; Cloutier, Y. Impact of Two Particle Measurement Techniques on the Determination of N95 Class Respirator Filtration Performance against Ultrafine Particles. J. Hazard. Mater. 2012, 217−218, S1−57.

(65) Kim, H. J.; Park, S. J.; Kim, D. I.; Lee, S.; Kwon, O. S.; Kim, I. K. Moisture Effect on Particulate Matter Filtration Performance Using Electro-Spun Nanofibers Including Density Functional Theory Analysis. Sci. Rep. 2019, 9 (1), 1−9.

(66) Bao, L.; Seki, K.; Niinuma, H.; Otani, Y.; Balgis, R.; Ogi, T.; Gradon, L.; Okuyama, K. Verification of Slp Flow in Nanofiber Filter Media through Pressure Drop Measurement at Low-Pressure Conditions. Sep. Purif. Technol. 2016, 159, 100−107.

(67) Shi, B.; Ekberg, L. E.; Langer, S. Intermediate Air Filters for General Ventilation Applications: An Experimental Evaluation of Various Filtration Efficiency Expressions. Aerosol Sci. Technol. 2013, 47 (5), 488−498.

(68) Kim, C. S.; Bao, L.; Okuyama, K.; Shimada, M.; Niinuma, H. Filtration Efficiency of a Fibrous Filter for Nanoparticles. J. Nanoparticle Res. 2006, 8 (2), 215−221.

(69) Matulevičius, J.; Klucininkas, L.; Prasauskas, T.; Buivydiene, D.; Martuzevičius, D. The Comparative Study of Aerosol Filtration by Electrospun Polyamide, Polyvinyl Acetate, Polyacrylonitrile and Cellulose Acetate Nanofiber Media. J. Aerosol Sci. 2016, 92, 27−37.