Journal of Membrane Science 531 (2017) 86–93

Contents lists available at ScienceDirect

Journal of Membrane Science

journal homepage: www.elsevier.com/locate/memsci

ALD-seeded hydrothermally-grown Ag/ZnO nanorod PTFE membrane as efficient indoor air filter

Shasha Feng[a], Dongyan Li[b], Ze-xian Low[c], Zhongyun Liu[d], Zhaoxiang Zhong[a,*], Yunxia Hu[d], Yong Wang[a], Weihong Xing[a]

[a] State Key Laboratory of Materials-Oriented Chemical Engineering, National Engineering Research Center for Special Separation Membrane, Nanjing Tech University, Nanjing 210009, PR China
[b] Chemical Engineering Department, Nanjing Polytechnic Institute, Nanjing 210048, PR China
[c] Centre for Advanced Separations Engineering and Department of Chemical Engineering, University of Bath, Claverton Down, Bath BA2 7AY, United Kingdom
[d] CAS Key Laboratory of Coastal Environmental Processes and Ecological Remediation, Research Center for Coastal Environmental Engineering and Technology of Shandong Province, Yantai Institute of Coastal Zone Research, Chinese Academy of Sciences, Yantai 264003, PR China

ARTICLE INFO

Keywords:
Formaldehyde degradation
Dynamic test
Indoor air filter
ZnO nanorods
Ag nanoparticles

ABSTRACT

It has been well recognized that there are a number of indoor contaminants including particulate matter, gaseous pollutants and microbials. The removal of indoor contaminants often requires multiple layers of various air filters. Herein, we report on a multifunctional air purifying filter produced by the hydrothermal growth of ZnO nanorod-wrapped PTFE nanofibers, constructed of nanostructured Ag deposited on the ZnO nanorods with a hierarchical structure for gas contaminant removal. Atomic layer deposition (ALD) was used to seed a layer of ZnO nanoseeds onto the PTFE fibrils which were then subjected to a hydrothermal reaction to form ZnO nanorods. Ag nanoparticels were subsequently assembled on the surface of the ZnO nanorods via a silver electroless deposition reaction. The resulting composite membrane exhibited an excellent dynamic antibacterial property of ~100% and a formaldehyde degradation rate of 60%. Compared with the pristine membrane, the gas permeation of the composite membrane increased from 227.26 $m^3\ m^{-2}\ h^{-1}\ kPa^{-1}$ to 275.36 $m^3\ m^{-2}\ h^{-1}\ kPa^{-1}$. The successful fabrication of this composite membrane with remarkable antibacterial and excellent formaldehyde degradation performance may provide a new route for the preparation of indoor air purification filters.

1. Introduction

A major component of modern-day indoor pollution is microscopic airborne solid material known as particulate matter (PM) or aerosols, which includes fine particles [1,2], bacteria [3–5], and hydrocarbons (toluene, xylene, formaldehyde and other organic components [6–9]). Among these, formaldehyde is one of the most prevalent pollutants in indoor air. These pollutants have serious environmental and health-related consequences that can cause adverse respiratory effects and even cancer [10]. Thus, it is of great interest to remove this PM, microbes, and formaldehyde from indoor air to help ameliorate these risks. However, conventional filters struggle to capture the fine dust with diameters lower than 0.3 μm, which is considered to be the most penetrating particle size (MPPS) [11]. Furthermore, bacteria contamination on the surface of commercial filters will inevitably lead to increased pressure drop across the filter and deterioration of the filter and its performance with the eventual release of microorganisms. In addition, conventional filters consist of multiple layers where each filter layer is able to filter only one particulate substance. They are incapable of removing formaldehyde from the air. Therefore, a multifunctional filter is needed for air contaminant removal with high PM capture efficiency and good antibacterial, and formaldehyde degradation performance.

The polytetrafluoroethylene (PTFE) membrane is one of the most commonly used filters for gas purification [12,13] thanks to its high gas flux, high chemical resistance and high water repellency [14–17]. In particular, the biaxial oriented PTFE membrane can be readily produced with good mechanical properties and a large amount of uniform micropores [12,18]. However, moist aerosols containing micro-dust and large amounts of microbes can cause pore blocking after filtration leading to a high pressure drop and low aerosol removal efficiency. Furthermore, the microbes accumulated on the filter will multiply rapidly, leading to poor air cleaning performance. Also, PTFE cannot be used for organic components degradation because PTFE

* Corresponding author. Nanjing Tech University, No. 5, xinmofan road, Nanjing 210009, China, Phone: +8613851715419.
E-mail address: njutzzx@163.com (Z. Zhong).

http://dx.doi.org/10.1016/j.memsci.2017.02.042
Received 24 November 2016; Received in revised form 14 February 2017; Accepted 27 February 2017
Available online 28 February 2017
0376-7388/

lacks catalytic properties. Therefore, much effort is required to design advanced filters that combine the advantages of high particulate removal efficiency, low pressure drop, excellent bacteria inhibition, and good formaldehyde degradation capability.

Materials with antibacterial properties have been used as antimicrobial coatings on various surfaces, and have included organic antibacterial agents such as chitosan, capsaicin and pyridine-based polymers [19–21], and inorganic anti-bacterial agents such as TiO_2, ZnO, Cu, Ag, and so on [22–25]. Among these agents, ZnO is a multifunctional material with good catalytic, electrical, photochemical and optical properties [26–28]. Also, ZnO is a semiconductor with a large band gap that satisfies the band edge potential requirement. The polar structure of ZnO renders fast separation and transport of photogenerated electrons and holes [29]. On the other hand, nanosized silver is known for its antibacterial properties for a wide spectrum of pathogenic bacteria. Also, nano silver has a light-harvesting couple and catalytic functions that may further improve the photocatalytic performance for degradation of formaldehyde under light irradiation [30,31].

In our previous work, we have reported two kinds of ALD modified PTFE membrane. While the ZnO nanorods (ZnO-NRs) functionalized membrane [32] was used for air purification with excellent superfine dust rejection rate (99.9999%) at a comparative low pressure drop (40% lower than pristine membrane). The amphiphobic PTFE membrane [33], which is further modified by grafting a layer of low surface free energy monomer through glow discharge plasma, was used for oil aerosol control. The oil aerosol removal efficiency of this membrane is greater than 99.5%. In this work, we report on a multifunctional air purifying composite designed filter that consisted of a hierarchical Ag/ZnO-nanorod-wrapped PTFE nanofibrous membrane. ZnO nanoparticles (ZnO-NPs) were first seeded onto the PTFE fibers by atomic layer deposition followed by hydrothermal growth of ZnO nanoparticles to form a nanorod array around the fibers. Ag nanoparticles were subsequently deposited on the surfaces of ZnO-NRs. The gas flux, dynamic antibacterial performance and formaldehyde degradation efficiency of the new composite filters were evaluated.

2. Experiment section

2.1. Materials

Porous PTFE membranes with a mean pore diameter of 5 μm in the form of circular disc (diameter: 47 mm; thickness: 100 μm) were purchased from Sartorius (Goettingen, Germany) and used as received. The ALD reactants were diethyl zinc (DEZ, 98%, MO source center of Nanjing University) and deionized H_2O, which were used as the Zn and O precursors. High purity N_2 (99.99%) was used as the precursor carriers and purging gas. Zinc nitrate hydrate ($Zn(NO_3)_2{\cdot}6H_2O$) and hexamethylenetetramine (HMTA, $C_6H_{12}N_4$) were purchased from Shanghai Lingfeng Chemical Co. Silver nitrate ($AgNO_3$) was purchased from Chinese Medicine Group Chemical Reagent Co., Ltd. All chemical reagents were of analytical grade and were used as received without further purification.

2.2. Deposition of ZnO seeding layers (ZnO-NPs@PTFE)

The dried PTFE membranes were placed in the chamber of a commercialized ALD reactor (SavannahS100, Cambridge Nano-Tech) and dried at the operating temperature for 30 min under vacuum (~1 Torr). Both the DEZ and H_2O were kept in the storage cylinders at room temperature. The generation of ZnO (in ALD process) is expressed by the equation:

$$Zn(C_2H_5)_2+H_2O = ZnO+2C_2H_6$$

In ALD, the substrate was exposed to alternating DEZ and H_2O reactants and the resulting membrane was formed stepwise. The substrates were deposited for 150 cycles at 130 °C with a steady N_2 flow rate of 20 sccm. In a typical ALD cycle, the DEZ and water vapor were sequentially pulsed into the reactor for 0.03 s. Immediately after each pulse of precursors, the system was purged with nitrogen for 30 s to sweep off the excess precursor.

2.3. Hydrothermal growth of ZnO nanorods (ZnO-NRs@PTFE)

ZnO-ALD PTFE substrates were immersed in a 35 ml aqueous solution with equimolar (5 mM) zinc nitrate and HMTA in an autoclave (70 ml, Zhenghong, China). The reaction was conducted at 90 °C for 3 h. Subsequently, the sample was recovered and washed with deionized water before drying in air.

2.4. Deposition of Ag nanoparticles

Two ZnO-NRs@PTFE and ZnO-NPs@PTFE membranes with diameters of 47 mm and a thickness of 100 μm were prepared and no extra pretreatments were performed on the membrane prior to use. Ag nanoparticles were deposited on the ZnO nanorods by an electroless silver mirror reaction. Briefly, an ammonia solution (2.5–2.8 wt%) was first added dropwise to 5 ml of a silver nitrate solution (2 wt%) until the precipitate completely dissolved to form $[Ag(NH_3)_2]^+$. Then, 3 ml of a glucose solution (10 wt%) was added. The ZnO nanorods@PTFE membrane sample was immediately dipped into the silver mirror reaction bath for 10 min at 50 °C. This was followed by washing the membrane with distilled water and completely drying it in an oven at 120 °C for 30 min.

2.5. Static antibacterial test

The antimicrobial efficiency of the filter medium was examined against (*Escherichia coli* (ATCC11303), *E. coli*). *E. coli* was purchased from Shanghai Seebio Biotech, Inc. The antibacterial performances were determined as follows: the microbial species were grown in broth solutions (Luria–Bertani broth for *E. coli*) for 24 h at 37 °C. The bacteria were harvested by centrifugation, washed with phosphate buffered saline (PBS), and then resuspended in PBS to a density of colony forming units per milliliter (CFU ml^{-1}). 100 μl of the freshly prepared bacterial suspensions was placed onto the surfaces of filters samples (3.0 ± 0.1 cm^2) under room lighting conditions. After 15 min, the sample was transferred to 10 ml of sterilized PBS and vortexed for 2 min to transfer the adherent bacteria into the PBS. The solution was then diluted serially and 100 μl of each diluent was placed onto agar plates (Luria–Bertani agar for *E. coli*). Colony forming units on the agar plates were counted under an optical microscope after incubation at 37 °C for 24 h. Each test was repeated for at least three times. The reported data were the average values of three parallel runs.

The antibacterial rate was determined by using the following formula:

$$\text{antibacterialrate}(\%) = \frac{A - B}{A} \times 100$$

where A (CFU) is the number of living bacterium in the control sample and B (CFU) is the number of living bacterium in the testing sample.

2.6. Dynamic antimicrobial test

The dynamic antibacterial test apparatus is shown in Fig. 1. The high concentration of bacterium liquid was first atomized using pure air through a collision nebulizer, then a sealed desiccator with full of silicone gel was used to dry the bacterium mixed air. The gas flow was controlled by a valve placed downstream from the gas cylinder. The gas velocity was maintained at 0.5, 1.5, 2.5, 3.5, and 4.5 cm/s. Two sampling ports were set before and after the membrane. The mixed air was run into a beaker containing a quantity of PBS, which had been